

HEAVY METALS AND COLLOID MOBILITY IN SOILS

By

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HEAVY METAL AND COLLOID MOBILITY IN SOILS

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Mobility of heavy metals in soils is of environmental significance due to their toxicity to both humans and animals. In general, heavy metal mobility is low because of its low solubility. However, enhanced heavy metal mobility has been reported under both laboratory and field conditions. It has been attributed to colloidal solubility of heavy metals and colloid-facilitated metal transport.

In this study, the solubility and mobility of heavy metals were examined in a Fe-spike and sandy soil and two Pb-contaminated soils. For the Fe-spike soil, water-flooded and non-water-flooded conditions were used to alter soil solution chemistry (e.g., pH, salinity), which were then treated with deionized water. It was found that Pb concentrations in leachates were related to the ratios of Fe concentrations in the leachates to Fe concentrations extracted with HCl. Enhanced Pb mobility occurred only when the Pb ratios were lower than a threshold value for a given soil. The two Pb-contaminated soils were incubated for different times under water-flooded conditions to alter their organic

status. Metal solubility was measured by analyzing the pore water of the incubated soil columns whereas metal mobility was measured by leaching the columns with 0.01 M CaCl_2 . The data showed that metal solubility in pore water and metal mobility in CaCl_2 solution were not always closely related. There has been sufficient evidence that a reduction in cation exchange capacity (CEC) occurs with Pb reduction (Boulet et al., 2000). However, the consequent redistribution of metals between solution and exchange phases with incubation was determined not only by the magnitude of CEC, but also the characteristics of metal ions, the competing anions and cations (Ap Dewi, 2000).

Colloidal mobility in the two Pb-contaminated soils was measured by analyzing the filtrates from 0.45 μm CaCl_2 in deionized water. In addition, a batch desorption test was conducted by dispersing the incubated soils in 0.01 M CaCl_2 and 0.45 μm CaCl_2 and then a release/solubility ratio (R) of an incubated soil was estimated from the desorption-time curves of its dispersion in the solutions. The results showed that colloidal mobility is greatly influenced by incubation and that colloidal metal mobility is enhanced when exchangeable Cu is easily replaced.

CHAPTER I INTRODUCTION

Understanding heavy metal migration is vital to accurately predict heavy metal mobility in contaminated soils is critical for assessment and assessment and cost-effective remediation (McCarthy and Anderson, 1993). Although much effort has been spent on developing models to predict heavy metal mobility in soils (Eisenberg et al., 1983; Sparks, 1984), these models often underestimate metal migration in soils. In most of the models, the interaction between dissolved metals and soil matrix is mainly described using a distribution coefficient (K_d), which is generally considered as a constant and usually measured in the laboratory under a particular condition. In a dynamic soil system, however, K_d is not a constant. In other words, solubility of metals and related mobility vary with soil conditions.

Besides dissolved species, mobile colloids can also act as vehicles to transport sorbed contaminants such as heavy metals in soils (Huang et al., 1993). Understanding mobility of potential heavy metal-bearing colloids is crucial for predicting the fate of heavy metals in natural porous media such as soil and aquifers (Stromgren, 1985; Ryan and O'Donnell, 1994) since colloidal particles are ubiquitous in these systems. In concept, the deposition and release of colloids in porous media can be described with the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory. However, it is difficult to apply to soil because of the heterogeneity and irregular dimensions of soil colloids. A colloid-facilitated metal transport model, COMET (Jahn et al., 1991), has been developed

or predict colloidal metal mobility. It is difficult to apply to soil environments because of the difficulties in determining the parameters needed in the model. It has been recognized that colloidal mobility in soil is mostly influenced by the physicochemical characteristics of colloids and soils (Jennings et al., 1991). Unfortunately, little is known quantitatively about the relationship between colloidal metal mobility and the characteristics of soil colloids (Auerbach et al., 1991; Jennings et al., 1995; Kaplan et al., 1997).

In this study, the mobility and stability of heavy metals, colloidal mobility and the interaction with heavy metals are studied. The main objectives of this research are as follows:

- To characterize the conditions at which enhanced mobility and stability of heavy metals occur with sorption on soils.
- To characterize the conditions at which enhanced colloidal mobility occurs with sorption on contaminated soils.
- To characterize the conditions at which enhanced mobility of colloidal heavy metals occurs with sorption on contaminated soils.

Therefore, there are two major subtopics in this dissertation, colloidal metal mobility and dissolved metal mobility (Figure 1-1). The understanding of colloidal deposition, release and interaction with heavy metals, is first presented and discussed in the next chapter. In Chapter 2, changes in colloid and colloid flocculated heavy metal mobility with sorption are examined in two contaminated soils. In Chapter 3, a fundamental approach is taken to relate colloidal mobility to colloidal stability ratio (R). A relative colloidal stability ratio is defined and measured by the curves of desorption time



Figure 1.1 A road-map of this dissertation

On the other hand, the effects of Pb solubility on soil and Pb-permeating behavior after incubation is examined in Chapter 3. In Chapter 4, co-experiments of the study from an uncontaminated soil to two Pb-contaminated soils is made (Figure 1-1).

CHAPTER 2 COLLOID DEPOSITION, RELEASE, AND ASSOCIATION WITH HEAVY METALS IN SOILS

Introduction

Colloid size-particles are ubiquitous in soil. It is well known that colloids may be mobilized and transported a significant distance (Ryan and Elmerich, 1986; Swenson, 1982) in soil environments. As a result, the mobility of heavy metals associated with the colloids may be enhanced (Kaplan et al., 1985; Anderson et al., 1983; McCarthy and Zechars, 1986; Newman et al., 1983; Miller et al., 1983; Ogungbese et al., 1986). Generally, colloid movement is faster than its parent macro-far in the effect of size exclusion (Shuster-Giveli et al., 1986). Therefore, colloid-facilitated metal transport has been considered as one of the important mechanisms causing heavy metals to move much faster than expected (Newman et al., 1982) which has attracted much attention in the scientific community.

The term colloid generally applies to suspended particles of 1 nm-1 μ m (McCarthy and Zechars, 1986), whose behaviors are size-dependent. Interactions among large particles (> 1 μ m, non-Brownian) are affected by physical forces, such as gravity and fluid drag, whereas those of submicron particles (1 nm-1 μ m, Brownian) are mainly controlled by the electrical characteristics of particle relative. Submicron colloids are of particular interest because of their significance in transporting contaminants that are



Figure 1.1. Schematic of potential energy profile of the interaction of radionuclides with various types of water molecules, electrical repulsion, and flow repulsion, which shows both primary and secondary minima and no energy barrier as well as the zones in which release and deposition take place.

large surface area and high porosity in porous media. Therefore, this discussion will mainly focus on subsurface colloids excluding microbes.

Since there is a collection of literature published on colloid release, transport and deposition in recent years (Ryan and Elimelech, 1999; Elimelech, 1995; Mills et al., 1991; Ouyang et al., 1999; Adamczyk et al., 1993; Kraljic et al., 1993; Elimelech et al., 1995; McCarthy and Zachary, 1989; McIsaac-Bayer et al., 1986), no attempt is made to present a complete critique on the topics. Instead, focus will be put on several parameters affecting the mobility of colloids and colloid-facilitated heavy metal transport in soils.

At the present time, various processes responsible for colloid deposition and release in porous media have been well established (Elimelech et al., 1995; Adamczyk et al., 1993; Kraljic et al., 1993; Elimelech et al., 1993; Ryan and Elimelech, 1999). These processes can be schematically described by the DLVO (Derjaguin-Landau-Verwey-Overbeek, 1952)-theory, which states that the net surface interaction energy is the sum of the interactions of electrical double layer (EDL) and van der Waals-London forces (WL), which vary with separation distance between particles. As particles approach each other, the net interaction energy experiences a secondary maximum first, then a primary minimum (β_{pm}) after a maximum energy barrier (β_{em}) (Figure 2-1). After the point, further movement towards each other causes drastic increase in the interaction energy, which manifested as a high force repulsion (Derjaguine, 1992). In principle, particles may be released or deposited when the net attractive forces are close to either the primary or secondary energy maximum. Both the magnitude of the energy barrier and the depth of the primary and secondary maximum are

affected by solution chemistry. In order for a deposited particle to be released, repulsive forces have to be generated between the surfaces of particles and stationary grains, as a result of changes in solution chemistry or fluid flow. However, the understanding of colloid release and deposition is far from complete. Colloid deposition under favorable conditions, in the presence of attractive interactions, can be predicted reasonably well, whereas colloid deposition under unfavorable conditions, in the presence of repulsive interactions, can not be predicted by the DLVO theory. In fact, colloid deposition rates observed experimentally are many orders of magnitude greater than those predicted and are independent of the size of colloid particles (Blanchard et al., 1993). Blanchard et al. (1993) have recently presented an alternative discussion on possible explanations for these discrepancies. However, compared to colloid deposition, colloid release is poorly understood, which will be emphasized in this review.

Transport of mobile colloids is a critical process for evaluating colloid mobility in soils. However, there are several extensive reviews on the topic (Blanchard et al., 1995; Chen, 1998; MacDonald-Boyer et al., 1994; Dequoy et al., 1994), so that topic is not emphasized in this review. Association of soil colloids with heavy metals has been an important issue for many years (McBratne, 1994; Joun et al., 1995), however, until recently, the attention has not been paid to the effect of such an association on colloid mobility (Kretzschmar et al., 1999a). In fact, in risk assessment widely used in the mining industry, it is well documented that aqueous heavy metals can be potential dominating part or specific adsorbing coat on charged surfaces of minerals (Frummerson and Palmer, 1990), therefore, such an association with charged surfaces may alter the

surface drops significantly. The potential impact of the environmental heavy metals with respect to colloid mobility will thus be amplified in the future.

More recently, Wang and Wilson (2004a,b) have demonstrated that colloid particles tend to adsorb onto the water-air interface as well and that the process is almost reversible. In fact, these findings have opened theoretical and experimental holes in the existing discipline (Williams and Berg, 1993). They concluded that colloid deposition onto the interface is an essential process outside most of the important mechanisms responsible for the retardation of colloid transport, except under extremely high flow rates that may drag the flocs in with the flow (Wang and Wilson, 1994a). Incorporating these results into a convective-diffusion equation, Coughrough and Chen (1994) have developed a model to predict colloid transport in unsaturated porous media. These results have substantially advanced colloid transport in technology fields; however, they will not be further discussed in this review.

Most of the current studies focus on either well defined porous systems (Clement et al., 1993; Tien, 1991) or subsurface aquifers (Soga and Elendeh, 1994; Iversen, 1993; McCarthy and Ewing, 1992). There is a significant model similarity between soil and subsurface or with defined porous systems. Different from the latter two, however, soil is more dynamic in its relative chemistry. Its surface soil pH, ionic strength, and water potential of soil solution are influenced by rainfall, humidity, and changes in land use whereas its redox state they are mostly impacted by the fluctuation in water table (Boul et al., 1997). In addition, as mentioned above, the gas phase is not negligible and the interfaces between colloid and air need to be taken into account along with that between colloid and water. Therefore, colloid transport is more dynamic and

complicated it is compared to that in solution. In this review, we will emphasize how wet environments affect colloid stability and what are the possible mechanisms.

The DLVO Theory

The classic DLVO-theory has been extensively used to describe colloid interactions and stability (Verwey and Overbeek, 1948). It has been extended to describe colloid deposition and release on porous media by including double-layer flow repulsion forces (Bokkariwar et al., 1974). According to the DLVO theory, the total interaction energy between colloids and stationary solid phases (ϕ_{total}) is the sum of electrostatic repulsion energy (ϕ_{el}), arising from the overlap of electrical double layers and attractive energy, ϕ_{at} , due to van der Waals-London dispersion, i.e., $\phi_{total} = \phi_{el} + \phi_{at}$, which is a function of particle separation distance. At close separation distances, a short repulsive force, the Stern repulsion, is also important. Thus, the generalized curve of interaction energy vs. particle separation distance shows two energy maxima (ϕ_{max}) & two minima (primary minimum (ϕ_{min}) and secondary minimum, Figure 2-1). Aggregation or coagulation occurs when particles collide with sufficient kinetic energy to overcome the energy barrier (ϕ_{max}) so that they reach a distance within the ϕ_{min} . On the other hand, if coagulated particles gain enough energy under perturbation to overcome the energy barrier ($\phi_{max} - \phi_{min}$) with increasing separation distance, they tend to be released. The shape, intensities and positions of the maximum and minima, are determined by the interactions between particle surfaces, which change with surface properties of particles and solution, and thus, interfacial characteristics.

In fact, significant discrepancies have been found between experimental observations and the predictions based on the DLVO theory (Furukawa and O'Melia, 1990). Therefore, in recent years, various updated theories of colloid stability have been proposed (Shikazono et al., 1985; Adamczyk et al., 1988). The accuracy of prediction has been somewhat improved using more sophisticated models in some systems. Nevertheless, stability and coagulation of clay colloids in solution can be qualitatively described by the DLVO theory in some systems (Norway and Quirk, 1988), colloid transport in solid porous media has also been qualitatively described using the theory plus the Born force (Bodemann and Friess, 1994). Although electrical interaction efficiency between colloids and porous media surfaces is much greater than the theoretical prediction (Furukawa and O'Melia, 1990), colloid deposition and release can be qualitatively described by the theory (Ray and Deenah, 1994a). Therefore, the concept of the DLVO theory is correct even though it is a simplification (Furukawa, 1990).

To reasonably predict colloid interactions in natural systems, the classic DLVO theory needs some modifications. Direct measurements of colloid interactions indicate other forces exist between particles (Israelachvili, 1992). The interactions between polar electron acceptors (Lewis acids) in solution and polar electron donors (Lewis bases) from colloid particles are termed AB forces and are usually dominant in aqueous systems as addition to electrostatic and van der Waals-London forces (Dux et al., 1998). It can account for up to 40% of interactions between and released particles in aqueous solution, so that the DLVO theory combined with the AB force adequately describes some nonclassical colloid stability (Dux et al., 1998; Wu et al., 1999a,b). One advantage of this approach is the AB force can be estimated simply by the contact angles between isolated

particles and liquids (Qin et al., 1988). Several common approaches are proposed to calculate the AB force using the formulae of Qin et al. (1988). The measurement needs to be made on at least three different liquids, two of which must be polar. In these approaches, the WL force (F_{WL}) can be estimated from surface tension instead of using assumptions for natural colloids as done by Ryan and Giddens (1996a) and Ray and Chaudhri (1996a). Here, the classic DLVO theory combined with the AB force is termed the extended DLVO theory. Besides the AB force, other non-DLVO forces between particles, such as van der Waals and steric interactions, should also be included. The extended DLVO theory should also extend the colloid surface roughness and heterogeneity of colloid components, shapes and sizes (Elimelech and O'Melia, 1996a,b). Unfortunately, no models yet successfully take all these factors into consideration. Nevertheless, the DLVO theory provides a solid foundation and a useful tool to describe colloid interactions (Elimelech, 1995; Ryan and Elimelech, 1999). Therefore, at the present time, it is practical to describe the interactions between colloids using the extended DLVO theory ($F_{DLVO} = F_{EL} + F_{VDW} + F_{AB}$). The extended DLVO theory has been more successful than the original one in describing colloid behavior (Qin et al., 1988; Wu et al., 1994a,b), which has been discussed in quantity the terms in the equation above by Qin et al. (1988).

As shown in Figure 3-1, in the presence of an energy barrier, the deposition of a particle from solution onto a surface is mainly affected by the magnitude and shape of the barrier extending from its maximum into the solution phase. These are primarily due to electrostatic, van der Waals-London and AB force contributions. In contrast, particle release depends on attractive or repulsive forces between the particle maximum and the surface, which is greatly influenced by additional repulsion of short repulsion (Orr

regions). Over this region, the energy profile is very sensitive to the specific characteristics of the interacting surfaces and intervening liquid layer. However, the regular dimensions of natural soil colloids make the interactions areas more exemplified, which will be discussed later.

The Characteristics of Colloids

Charge development

Solid particles present in water are often charged. The mechanisms of charge development have been extensively investigated (Parks, 1963; Sumner, 1982). In general, based on the nature of solid particles, charge development can be divided into three categories: (1) ionic substitution is most common in soil clay particles and referred to as permanent charge; (2) specific chemical interactions between surfaces and solvent, including hydrolysis of surface functional group (e.g., hydroxyl and carboxyl) and chemical adsorption; and (3) preferential dissociation resulting from preferential hydration of surface cations. In addition, based on the contribution from electrolyte in solution to the charges of particles, one can be classified into three categories: potential determining ions, specific adsorbed ions and indifferent ions. Potential-determining ions are the constituent ions of solid particles (e.g., H^+ and OH^- for Fe oxides, Ca^{2+} and CO_3^{2-} for $CaCO_3$) and their concentrations determine primarily the surface potential of particles (Parks, 1967). Specific adsorbed ions are ions that give the magnitude and sign of the surface charge (e.g., Ca^{2+} , Pb^{2+}) by interacting with the surfaces and forming a Stern plane or electric double layer (EDL)-theory (Parks, 1977). Indifferent ions adsorb physically to surfaces and change the magnitude of the surface charge (e.g., Na^+ , Cl^-), and from a

diffusive layer in ECL, resulting from a balance of these electrostatic and steric interactions with the surface and bulk solution (Parks, 1973).

In soils, however, colloids are heterogeneous in composition. They generally consist of inorganic and organic constituents. Heterogeneity in the composition and structure of colloidal particles make their charge development a complicated matter. This may be further complicated by the dynamic nature of soil solution chemistry, which may cause colloid composition and structure to vary temporally and spatially. Nevertheless, numerous studies have shown that the charge-developing process can still be described using the ECL theory, at least in principle.

Electrical double layer (EDL) in metal oxide-mineral interfaces

Electrical double layer of a dispersed particle consists of a charged surface and a diffuse layer of counter-ions near to the surface based on the double layer theory. Since soil studies may play an important role in colloid stability and have been well characterized using various methods of soil-related parameters (Schulze and Stumm, 1983; Dzombak and Morel, 1990), we use them as an example. When specific adsorbing ions other than H^+ and OH^- are shown in a system, the charge-developing process on the surfaces can be described as follows (Schulze and Stumm, 1983):



Where SOH denotes a surface site and $K_a^{H^+}$ and $K_a^{OH^-}$ are the intrinsic surface acidity constants and defined as follows:

$$K_a^{H^+} = [SOH_2^+]/([SOH][H^+]) \quad (2-3)$$

$$K_a^{OH^-} = [SO^-][H^+]/[SOH] \quad (2-4)$$

Schindler and Stumm (1987) summarized the intrinsic acidity constants (K_a^{int} and K_a^{ext}) of various metal oxides and found that the constants are generally correlated to those in solution. However, the acidity of protons in the surfaces of metal oxides is much more complicated and influenced by changes in surface composition and structure (Toor et al., 1979; Sanyal, 1994; Blum, 1995). In addition, the values of these constants depend on the particular electrostatic model adopted, such as constant capacitance, diffuse double layer and triple layer. However, the form of Eq. (2-1) and (2-3) can be expressed as follows:

$$\text{pH}_0 = \text{pH}^* - \log K_a^{\text{int}} \quad (2-5)$$

Eq. (2-5) is simply related to the point of zero charge (PZC or pH_0), which is experimentally measured and is independent of electrostatic models for the solid-water interface. When the concentration of positively charged surface species is equal to that of the negatively charged (i.e., a zero charge surface), the pH_0 is related to the intrinsic equilibrium constant:

$$\text{pH}_0 = 0.5 \log K_a^{\text{int}} + 0.5 \log K_a \quad (2-6)$$

Eq. (2-6) states that intrinsic acidity constant (K_a^{int}) is equal to the apparent acidity constant (K_a) at a surface potential of zero. It not only indicates that pH_0 is a measure of K_a^{int} but also raises the question that the binding of protons on metal oxide surfaces is more analogous to the binding of metal complex in an aqueous phase (Schindler and Stumm, 1987) or in bulk crystal structure (Sanyal, 1994). The correlation between the surface acidity constants of metal oxides and those in solution support the former point. However, the surface ion exchange is substantiated for some mineral particles (Schindler and Stumm, 1987). More recently, Blum et al. (1995) recommended

thermodynamic data for the adsorption of protons on metal (hydr)oxides. They found that the enthalpy values calculated with K_{a1}^{int} and K_{a2}^{int} are very similar and are much lower than those of the hydrolysis of aqueous metal ions. This is consistent with Lythgoe's work (1974), in which he describes the adsorption of potential-determining ions as a process characterized by a single enthalpy value instead of two. These indicated that it is unrealistic to represent acidic, neutral, and basic surface groups using Eqs. (2-1) and (2-2). The active surface site may be a surface metal complex and reaction (5) (OH_{int}/OH_{ext}) (n_1 and n_2 being the stoichiometric index of pH) offers a better description of the involved processes, for $pH < pH_0$, $n_1 = n_2$, and $n_1 < n_2$ for $pH > pH_0$, $n_1 = 0$, and $n_2 > 0$. In fact, the existence of adsorbed water molecules and surface hydroxyl groups has been observed experimentally (Tyrkka-Tyrkka and Aantaa, 1988). Based on this notion, the surface participation in the displacement of OH⁻ with H₂O resulting in an increase in the number of coordination (Johansson et al., 1998), which can explain why the enthalpy of protonation is smaller on either side of pH₀. Further, Chen et al. (1999) have pointed out that there is a difference in Gibbs free energy between forming aqueous metal ions and surface metal complexes, and inferred that the difference may have resulted from the dehydration of the adsorbing ions. They argued that in the adsorption, adsorbed species should occupy kink, edge position, or active positions, where water molecules from the first coordination sphere must be removed. They concluded that the easy dehydration of metals species should account, at least partially, for the observed difference in the hydrolysis in solution and the surface complex. These results suggest that the solvation of metal ions must be included. Following this line and considering crystal chemistry (Fukui, 1960; Yano et al., 1978) and adsorption theory (Gurevsky,

1991). Sreepathy (1994) has shown that surface potentials on a wide variety of minerals can be accurately calculated from the dielectric constant of the solid and the ratio of the Pauling bond strength to the average hydrogen bond length of the solid particles. This suggests that such more complex should be placed as the analogy between the bonding of the surface protonated species and the bonding in the underlying crystal structure. In Sreepathy's approach (1994), the properties of crystals have been normalized with its electron quantum number of the quadrupole terms such as kinks, edge position, or surface position. The details on modeling of calcareous pHs can be found in the literature (Parks, 1984; Yoon et al., 1979; Sreepathy, 1994; Blum, 1993).

Parkash et al. (1987, 1989) have demonstrated that pH- and temperature-composition exist as the surface charge developing processes of various metal oxides. In a systematic series of experiments in which the surface charge σ_0 of a number of oxides [TiO_2 (rutile), Fe_2O_3 and $\alpha\text{-Fe}_2\text{O}_3$ (hematite)] in aqueous solutions of KNO_3 was measured as a function of pH, ionic strength and some other variables. When σ_0 is plotted as a function of $\text{pH}-\text{pH}_0$, where pH_0 is the PZC, the curves coincide for the three oxides at three ionic strengths even though they are different at pH_0 . In other words, the individual identity of metal oxides makes no difference to the U-shaped plot of σ_0 vs. $\text{pH}-\text{pH}_0$. Similarly, in the measurements of the temperature dependence of surface charge development, changes in temperature only affect the positions of PZC, not the trend of the surface charge developing process. They conclude that the electrical double layer on metal oxides can be functionally divided into a specific and a generic part, with respect to the nature of oxide and electrolyte. The specific part, which is determined by the specific interaction of a surface with process in solution, determines the PZC. This is

consistent with the result of Srebnitsky (1994) is accepted. The general point, which is controlled by the relative size of the double layer, determines the surface charge development once the surface charge deviates from pH_0 . It can be described well by the Helmholtz law ($q_{\text{HL}} = 1.366 \cdot 10^{-4} (pH - pH_0)$). The significance of this analysis, first, that it has provided a thermodynamic basis for double layer model that divides the charged interface into a charged surface and a diffuse layer near the surface, second, that the Helmholtz law is believed to describe the charge developing processes at all scales. It has been recognized that the Helmholtz Equation is valid only when the electrical potential of H^+ in interface is a constant (Blesa, 1994). In a practical sense, the potential can be treated as a constant if the amount of H^+ in the interfacial layer is much higher than a charge carried by the charge-developing process (Blesa, 1998). However, for metal oxides only 1-10 sites per 100 Å ($\sim 10^{17}$ sites m^{-2}) are usually found (Sigg et al., 1997) and as the experimental pH range spans up to 80% of the sites may be charged (Blesa, 1994). Therefore, if the solution of the binding site $SiO_4H_4O_8(OH)_2O_2$ set discussed above is more representative of the real site on metal oxides compared with $SiOH$, adsorbed protons can be considered into neutral groups (SiO_2) on surfaces, and thus the adsorbed H^+ would not change much with surface charge. This may result in the Helmholtz behavior.

In the presence of specific adsorbing ions ($SiOH$) such as Ca^{2+} and Mg^{2+} in solution, the charge developing process becomes more complicated (Lythkens, 1994; Arduini, 1993). Generally, the PZC will be shifted compared with the one in the absence of these salts. Lythkens (1994) defined the PZC curve in the presence of $NaCl$ as a point at which H^+ and OH^- are just balanced at the surface. This is equivalent to the surface charge $q_s = F([H^+]_s - [OH^-]_s)$. The requirement for the definition is the dominance

ammonium of oxides to H^+ and OH^- . Consequently, SiO_2 behaving as the Lewis charge. Therefore, the PZC in the presence of SiO_2 remains fully defined by their definition. PZC is still thought where $\alpha_0 = 0$. If the cation adsorbs on to the large layer PZC is lower than the PZC in the absence of SiO_2 because cations in the small layer favor the adsorption of OH^- over H^+ , so that a lower pH is required to restore the $H^+ - OH^-$ adsorption balance. Similarly, specific adsorption of anions leads to PZC's above the present value.

In fact, in the presence of SiO_2 , the constant intersection point (CIP) of titration curves with various ionic strengths has also been observed. Similar to the situation in the absence of SiO_2 , the CIP is the equal compensation point (Lythkens, 1984), at which charge-compensating cations and anions have an equal affinity to the surface. From this point of view, they explained CIP of PZC in the case of specific adsorption as follows: at the PZC, adsorption of cation cations are favored over that of anions if cations have a higher affinity to the surface. In order to reach a situation where the cations adsorbability of cations and anions is identical (equal compensation point), a positive charge on the surface has to be developed. This charge should be more positive with higher specific affinity of cation to the surface. Once the equal compensation point has been reached, further increase in concentrations of cations and anions do not lead to further shift, i.e., all successive curves intersecting concentrations must pass through the point. Similar reasoning applies to a situation, which cations have a higher affinity over anions. This principle is important to understand the legend of red oxides chemistry on soil colloid charge development. Following this point, it is easy to understand the effects of changes in species of cation and anions in solution on PZC and CIP.

In the discussion above, we have been dealing with well-defined crystal surfaces, in which the desorption can be explained using surface complexation equations. However, solubility of coral skeletons has to be taken into account, especially in the case of amorphous hydroxides. Under such conditions, the adsorption and desorption of the hydrolyzed metal complex has only become an alternative to determine surface charge other than the surface complexation of H^+ and OH^- . Based on the maximum solubility theory (Parks et al., 1982), PSC should be related to the isoelectric point (IEP) of an aqueous solution depending on the particle. The IEP is defined as the pH resulting from an equivalent concentration of positive and negative complexes in aqueous phase (Parks, 1982), which is often found as the pH of maximum solubility of a solid. Bawa et al. (1991) have found that the PSC and IEP for metal oxides do not always coincide; however, the deviation from IEP ($PSC - IEP$) can be explained well if considering the fact that the complex cations and anions require different dehydration energy when they are transferred from solution to surface. They explained that monomeric cations hydrate more strongly than anions in aqueous solution, so the shift should be small and negative when the charge is determined by monomeric surface complexes and the maximum solubility theory is generally valid. On the other hand, for polymeric species more specific behaviour can be expected. Relative large positive or negative shifts may result if the charge surface complexes are polymeric. Obviously, the underlying assumption of these approaches is that the surface active site is more analogous to these solution species. This may be more suitable in soil environment where various amorphous minerals are abundant and aqueous species are more undissolved than surface species.

Charge development at soil particles

In general, surface charge of soil particles can be classified into two types: permanent and pH-dependent charges. Detailed characterizations of soil particle charges have been developed by Charles and Sposito (1987), Anderson et al. (1993) and Chao and Sposito (1995). Charge-developing processes on soil particles are more complicated than those on metal oxides because the surface composition and structure of soil particles varies greatly and PZHCs are not linked to just H^+ and OH^- . However, similar phenomena such as CIP have been observed, which is referred to as the point of zero net-charge (PZNE). It is often found that PZNE deviates from CIP (Chao and Sposito, 1995).

Soil is a mixture of various minerals and organic substances. Further, there can be significant amounts of amorphous materials, such as amorphous Fe and Al. It is well documented that the existence of hydrolyzed species of Al and Fe have significant impact on the pH-dependent charge of soil particles (Chao and Sposito, 1995; Pabst et al., 1999), and these may increase with organic matter. Further complicates the charge-developing process (Chao and Sposito, 1995). In addition, mineral dissolution may be significant for some soils and may affect the charge-developing process greatly (Jiang et al., 1997). Combining all these factors with the dynamic nature of solution chemistry, one may conclude at the present time it is impossible to accurately predict precise surface charge-developing process.

In principle, however, Jona et al. (1990, 1997) is more promising. They emphasize the role of partitioning of charged species between solid surface and solution during surface charge-developing processes, which is driven by the difference in Gibbs free energy between a charged species in solution and on surfaces. The underlying

assumptions of this approach is that the charged species in solution and on surfaces are similar. This approach has relatively sound theoretical basis and is consistent with experimental evidence.

Clays development in arctic soils

Considerable amount of research has been conducted to understand clays development of water dispersive and mobile colloids (Gill et al., 1999a,b; Kortelevans, 1991-1994). It is commonly observed that the mobility of colloidal clays in soils is many times greater than that of non-dispersible reference clays. Also, clays isolated from surface soils were found to be more dispersive than clays from the subsurface horizons of landscape such as the Southwestern USA. Factors contributing to the high dispersibility of soil clays include the presence of adsorbed organic matter, cationic quantity of cations in landscape clay, and larger surface roughness of soil clays compared with unweathered reference clays.

Organic matter is an important aspect of negative charges in soils. Well decomposed human manure has a CEC > 300-cmol kg⁻¹ humus, which is considerably greater than that of clays such as kaolinite (3-15), illite (30-40) and montmorillonite (30-100). It has been estimated that 20-50 % of the CEC of many soils originates directly to the soil organic matter alone (Singh et al., 1994; Stevenson, 1982). In soils, dissolved organic-matter (DOC) tends to adsorb onto solid particles such as clays and metal oxides, which is driven by ligand exchange, multivalent ion-binding, Van der Waals force and hydrophobic interactions between DOC and the solid minerals (Murphy et al., 1995). In particular, for Fe and Al oxides, when the pH of a system is lower than their PZC, adsorption of DOC onto the minerals increases significantly because of the electronegative

interaction between the ions, resulting in a significant impact on their surface charge.

There are numerous studies of the effects of organic coating onto metal oxides (Tipping *et al.*, 1982) and clay minerals (Kinniburgh, 1996) on surface charge. Hird and Sparks (1983a, b) found flocculation of silica and colloids with organic coatings increased with pH in Ca solution, which is contrary to their flocculation behavior when organic matter is removed by H_2O_2 . They concluded that the competition between protons and Ca onto the acidic functional groups of organic molecules is essential in the charge development on metal colloids. A similar result was also found by Kinniburgh (1992, 1997) on humic-coated kaolinite and clay. On the other hand, it has been reported that the electrical properties of the quartz surface dispersed in water (Chiang-Boeck, 1982) is determined essentially by their interactions with inorganic cations such as Al and Ca instead of organic matter (Frostley *et al.*, 1994). In concept, however, these results are consistent with others, i.e., surface electrical properties of minerals are a result of interactions both in the interface of particle-solution and in solution, including particle-particle interaction, organic-inorganic ions, particle-inorganic ions, etc. Particularly, types of cations, such as protons and multivalent cations, and their concentrations are important for the charge development on particles in solution in aqueous media.

It is unrealistic to model surface charge development on soil particles with reasonable certainty at the present time. However, it is evident soil particles can be treated as assemblages of crystalline and amorphous minerals and organic molecules. Simplified models such as the triple layer model do not make much sense in describing the diversified interfaces of such particles considering that the particle surfaces are irregular and the Stern layer often moves inward inside of the physical boundary of

the particles. As a first approximation, on the other hand, the interface of solid particles is more reasonable described by diffuse double layer with a specific part $i < i_0$ a charged surface and a general part $i > i_0$ a diffuse layer. The surface charge developing process may be described by the partitioning of charged species between solution and surface assuming the charged species are identical between the two phases.

Discussion

Water molecules may be organized surrounding the immersed particles, forming 'Hydration shells' (Culford, 1975). Once like particles with such shells approach each other, additional forces between the particles arise. The origin of these forces is the interaction between polar electric dipoles (Lorentz shells) in water and polar electric dipoles (Lorentz forces) from colloidal particles, and termed *AB* forces as discussed previously (Ooi et al., 1981, 1985). Surface electric density of colloid particles is critical for water molecules to be oriented along the surface. Strong surface electric density causes water-orienting of water molecules orienting along the surfaces, resulting in a repulsive force between like particles. Weak surface electric density causes less orienting of water orienting, resulting in non-repulsive force. Ooi et al. (1986) have demonstrated between particles dispersed in water the interaction free energy from *AB* forces appears to increase, or decrease, as strongly as much as 150 times greater than *EW* energy and 10 times more than greater than *EL* energy at close range (1-5 nm). It can account for up to 10% of the interactions between mineral particles in aqueous solution, such that the DLVO theory combined with the *AB* force can adequately describe some monodisperse colloid stability (Ooi et al., 1985; Wu et al., 1994a,b). Wu et al. (1994a,b) have experimentally evaluated the interactions between the particles of montmorillonite and

solute by excluding flocculation of their suspensions while increasing Ca^{2+} concentration. They concluded that Ca^{2+} not only causes a decrease in particle ζ -potential, but it also chemically lowers the electric density of the outer surface of the particles, resulting in an AB attractive force, which is more responsible for the flocculation of the suspensions. Obviously, salts such as Ca^{2+} alter not only ζ -potential when it adsorbs onto a particle, but also decreases the surface electric density. This result means that surface electric density and ζ -potential of particles are related.

Size development of mobile colloid

The behavior of colloids are size-dependent. Individual colloidal particles may aggregate depending on the magnitude of the energy barrier of their interaction (Figure 3-1), which is similar to colloid deposition that will be discussed later. Briefly, if the energy barrier of interaction is low, fast coagulation occurs, in which case the diffusion rate of colloids is the limiting factor; the aggregation rate is otherwise controlled by the interaction of colloidal particles. These two mechanisms result in lower and higher final distributions of aggregate sizes, respectively (Rutledge et al., 1990). However, direct measurement and theoretical simulation of colloid size distributions in natural systems have shown that the concentration of colloids $< 2\text{--}4\text{ }\mu\text{m}$ should be negligible because of their almost instant coagulation (Flindt et al., 1983; Buffle et al., 1985). Kaplan et al. (1987) examined the possibility of aggregation of mobile colloids from a reconstructed soil profile. They analyzed the size distribution of particles in the suspensions with and without coagulation, which is supposed to break down aggregation in the suspensions. They found that the suspension without coagulation exhibits almost the same bimodal particle-size distribution as the one with coagulation. This holds the soil suspensions

colloidal fines are different soils - clayey sand and sandy soil in Southeastern USA. These results suggest that colloid aggregation in pore pore space is very limited especially when soil colloid particles are highly charged (Kaplan et al., 1993, 1997). Interestingly, similar bimodal size distribution of mobile colloids has been reported by Brown et al. (1992), who characterized the suspended particles collected from groundwater as a mixed phase, phenolic copolymer of latex. Kaplan et al. (1996) explained that smaller particles are less likely to be retained during transport in porous media based on the *steric hindrance theory* (Hsu et al., 1987). This suggests that, in the bimodal distributions, colloids of smaller size ($< 0.4 \mu\text{m}$) may have resulted from long-distance transportation to sampling point, while those of larger size ($> 1 \mu\text{m}$) may come from local deposition at the sampling point.

The Characteristics of Colloidal Media

Colloidal colloids interact with the surfaces of porous media, which is more important than those between colloids in natural pore space. Therefore, pore structure and the physical-chemical surface characteristics have tremendous influence on colloidal mobility. Extensive studies have been done on the systems consisting of these surfaces of porous media (Adegoke et al., 1985; Kelley et al., 1987; Elimelech et al., 1993). However, large discrepancies in colloid deposition rate under colloidal deposition conditions between theoretical predictions and experimental observations have been found. This has been attributed to the hydrodynamic effect and surface heterogeneity of the porous media, such as surface roughness and local charge heterogeneity. This has been considered to be the most promising approach to understanding the interactions between colloids and porous media in above systems (Jiang et al., 1994). There are many

colloidal structure on this topic (Gronow, 1995; Ryan and Chaudhry, 1996; Chaudhry, et al., 1999).

In a soil system, the porous media is an assemblage of a wide range of particles, which vary greatly in morphology, surface composition and distribution. Different from pure systems, where the surface properties of porous media may be far different from those of colloids, the surfaces of soil porous media may at least in part consist of potentially mobile colloids. In sandy soil, a small amount of clay-size particles tends to pack closely along large sand grains driven by energy minimization. This arrangement among a grain and colloidal particles has also been confirmed by theoretical analysis (Zabala et al., 1991). Based on this fact, the interactions between colloids and porous media can be treated as those between colloidal particles, as a first approximation, which has been a long-established concept. Brenner (1982) has suggested that in an undisturbed soil profile, the entire site of the porous media may be completely occupied by mobile colloids. Ryan and Chaudhry (1996) have successfully related the observed colloid release rates from an Fe oxide-coated sand column to $\exp[(\phi_{\text{colloid}} - \phi_{\text{solid}})/\phi_{\text{colloid}}]$. Their estimation of the energy barrier $(\phi_{\text{colloid}} - \phi_{\text{solid}})$ is based on the interactions between colloids rather than those between colloids and porous media surface. The underlying assumption is that porous media surfaces are identical to colloid surfaces.

Deposition of Colloids

Theoretical background associated with porous media

Colloid mobility through porous media is usually determined by the net rate of colloid deposition and release. Generally speaking, deposition of colloids onto porous

media can be viewed as a two-step process: the transport of solids from bulk solution to the proximity of the surface and then their attachment to the surface, which depends upon the nature of particle-surface interactions. If the energy barrier (ϕ_{bar}) is $\leq k_B$, the flux of solid/transport is equal to that of deposition. In other words, the collection efficiency of the collector (given media) is 100%. The energy barrier ϕ_{bar} must overcome the energy barrier for a collected particle to attach to the surface (Figure 2-1). Therefore, deposition rate constant (k_{dep}) is related to the energy barrier ϕ_{bar} with $k_{\text{dep}} \propto \exp(-\phi_{\text{bar}}/k_B T)$ where k_B is the Boltzmann constant and T is absolute temperature (Quake et al., 1994). The major mechanisms of solid/transport to a collector are: contact impaction, interception, sedimentation, electrostatic forces, Brownian diffusion, and gravity. Collection efficiency contributed from each of them has been described by Tien (1995) and the details will not be repeated here. In porous media, however, many factors mentioned above may be operative simultaneously. The overall collection efficiency can be theoretically calculated based on the filtration theory (Tien et al., 1991). However, the great discrepancy between prediction and experimental observation under collectible deposition conditions has been observed. This has been attributed to the distribution of surface and physical properties, surface charge heterogeneity of solids, surface roughness, low liquid electro-dynamics and solid deposition in secondary minima (Jaramideh et al., 1995). In order to take this discrepancy into account, collection efficiency ($\alpha = \eta/\eta_0$) is used, where η and η_0 are observed and calculated collection efficiencies, respectively. As particles deposit on a collector after several steps, the deposition rate will change depending on the nature of particle-particle interaction. If the net interaction is repulsive, the collector surface becomes progressively excluded as

particles accumulate and colloid-deposition rate declines accordingly. This surface exclusion phenomenon is termed blocking. There are some excellent recent reviews on this topic (Ryan and Elwood-Jones, 1996; Elwood-Jones et al., 1996; Swenson, 1998).

Colloid deposition in soil

Transient phenomena in colloid deposition. There are no clear or pure surfaces in soils. Therefore, the results obtained in well-defined porous media cannot be directly extrapolated to describe colloid deposition in soils. In fact, in any given time or zone in soils, the most favorable deposition sites are likely to quickly be occupied. Alternatively, if there is influx of mobile colloids as a result of some abnormal or mechanical disturbance, there may be lateral deposition during the early stages of exposure. This occurs because favorable deposition sites are already filled, which is different from clean porous media. Over a prolonged period of exposure the α colloid flux, on the other hand, and porous media may develop surfaces that are more similar to those of mobile colloids (Gronwald, 1999), which has been discussed before. In soil porous media, therefore, colloid deposition may be a transient phenomenon.

Dependable fractions of soil clay resulted from vigorously shaking in water can be a reliable measure of the amount of potentially mobile colloids. Miller et al. (1989) observed the amount remaining in suspension after 24 hr of shaking was highly correlated to surface soil loss at the Southwester 1.5 water high velocity rainfall. Kaplan et al. (1987) have found mobile colloids from two soils are similar in morphology to the water-dispersible clay and that they are many orders of magnitude lower than the amount of water-dispersible clay in the soils. In other words, there is significant amount of

potentially mobile colloids loosely attached to the soil particle surface, however, during this period they function as a part of stationary porous media. They may be detached from the porous media (colloids) once they are exposed to a chemical or hydrological perturbation. I have referred to this stage a transient phenomenon as colloid dependent. In fact, there are a few examples in soil, however, it has to be emphasized to understand the distinctly different features of colloid mobility in soil porous media. Take carbon soil, for example. A perturbation such as rainfall occurs on the soil surface and moves downward. Such a perturbation may result in a release of deposited colloids, and then the mobilized colloids move down over the surfaces of porous media avoiding of the deposited colloids. Therefore, at the front of the downward-moving perturbation, there are two opposite processes operating simultaneously: deposition and release of soil colloids. The former is mainly influenced by the blocking effect, and the latter will be discussed in the following section.

Size screening as a restriction. If the effective size of a colloid particle is larger than the smallest pore through which flow is flowing, the particle is retained by porous media, which is referred to as size screening. Restricting motion or gradual bed filtration of the ratio of the compressed particle diameter to the pore diameter is greater than about 0.2 (Huang et al., 1992). Retention is one of the most important mechanisms of colloid deposition in soils (Jena et al., 1987; Macfarlane et al., 1987; Kaplan et al., 1987). Jena et al. (1987) have examined the permeability of water dispersible clay through compacted columns and found that size screening is an important factor in determining the concentrations of colloids in leachates along with pH, small exchangeable bases, cation exchange capacity, organic carbon content, etc. They concluded the relative flow colloid

transportability is attributed to larger colloid mol. wt. and more streaming. The streaming may manifest itself in another way. Jacobson et al. (1997) examined the transportability of silica through and retention occurring macro pores, and found that macroretention occurring through soil-colloids are negatively related to the sizes of various macropores in soil columns. However, no significant difference in mobility through the columns between the silica modified coarse sand (humic acid) and non-treated. This suggests that streaming is the predominant process in determining the deposition over the non-pore coated and coated media, resulting from the coatings of humic acid. In their study, this is further confirmed by the fact that colloid concentrations in leachate increase with the intensity of salinization, as they argued, a high intensity of salinization negates the effect of streaming. However, this is contrary to the results of Kertész et al. (1995). Kertész et al. (1995) found no leachate coated with humic acid results in a much lower collection efficiency in columns packed with "clean" sorption particles. In fact, it is this contradiction that demonstrates the difference of colloid deposition between soil porous media and clean porous media. Thus streaming may be a dominant mechanism of blocking effect in operation in soil.

Release of Colloids in Soil

Different from colloid-deposition, which is essentially described by the interactions at larger separation-distances, colloid release depends on interactions at separation between the primary maximum-sized soil surface (Figure 3-1) and is greatly influenced by colloidal repulsion at short separations. Colloid release is generally expected when the repulsion is generated between porous media and colloids. The

efficiency of colloid release depends on whether the process is caused by diffusion alone or by an applied external force (Kallay et al., 1987). Without external forces, the rate of particle release is proportional to the diffusional escape probability of the deposited colloids through the energy barrier, i.e., the energy well $(E_{\text{max}} - E_{\text{min}})$. It is otherwise determined by the shape of interaction energy profile between surface and the primary energy maximum (Figure 3-1) as well the smaller the slope (height) of the curve the less force needed for colloid release, where h is the separation distance. Up to this point, it is clear that the two opposite processes, colloid deposition and release, are controlled by different mechanisms and factors. For a given system, colloid colloid concentration is dominated by the relative magnitude of colloid-deposition and release rates. The residence time of colloid-carrying solution in the system also plays an important role. A longer residence time represents a condition closer to the equilibrium of colloid deposition and release, while a short one may dominate deposition over release and vice versa. For example, colloid deposition in batch experiments, in general, is a result of balancing between colloid-deposition and release because of the longer residence time. In general, whereas colloid release from a short column may be free of redeposition release. Therefore, one must take extra caution when extrapolating colloid stability obtained from batch experiments to colloid transportability in column experiments, where kinetic effects are more pronounced.

In a real case, one can measure energy profiles for various colloids deposited on Figure 3-4 due to the heterogeneity of colloids and surface media. Each energy profile represents the interaction between a individual particle at a specific location on porous media. For simplicity, we imagine that there are two smaller energy wells

groups based on similarity, made of three lumped profiles representing the interaction of a group of similar particles with porous media with \pm -correlated morphology and position of the energy maximum and minimum. Therefore, the deposition and release of soil colloids may manifest themselves as a strong chromatographic pattern (Chapter 9).

The release of colloid solutes

Similar to colloid dependent, colloid release rate is generally determined by both colloid detachment from porous media and transport to bulk solution. Ryan et al. (1994a) examined the release rates of colloidal humic acid from heparin-coated sand columns under different ionic strengths and flow rates. They found that colloid release rate decreases as ionic strength increases, which was supposed to reduce the size of the energy barrier. In addition, colloid release rate also decreases with increasing flow rate, which is contrary to the expectation that a greater mobilization would occur at a greater flow rate due to greater hydraulic shear on deposited colloids. They suggested the rate-limiting step in colloid release is the transport of detached colloids to the bulk fluid where rapid colloid release corresponds to conditions where the energy barrier has vanished from the potential energy profile. Coincidentally, a similar phenomenon has been observed by Jacobson et al. (1997) in column and column experiments where natural particles are treated with tap water. Their results showed particle mobilization is not influenced by increases in flow rate. Further, the plot of normalized amount of mobilized particles versus square root of time shows a fairly linear release implying diffusion limited kinetics. One possibility for diffusion kinetics being dominant is the lower maximum of mobile colloids numbers, which may be very common in soil because of the transient phenomena discussed before. The lack of flow rate effect in the

later study may be caused by the smaller slope of energy profile (Figure 3-4) for potential mobile colloids in the gassy condition, which may be overcome by heteroion electrolyte, cation, subsequently, these potential mobile colloids become truly mobile. Therefore, colloid dilation is efficient only to compensate by its movement from stabilizing more potential mobile colloids by increased flow rates. This is based on the heterogeneity of the interactions between colloids and media at soil.

Mobile colloids and water-dispersible clay

Kaplan et al. (1993, 1994, 1997) examined extensively the release of colloids from an Illinois in the southeastern coast of the U.S. Mobile colloids were collected during and after acid rain events from the reconstructed pedon. They found the mobile colloids are similar to the water-dispersible clay in morphology, which is consistent with the results reported by Sato et al. (1997). However, there were some differences. Kaplan et al. (1997) found that the mass and composition of the mobile colloids differed from those of the water-dispersible clay, with the former being smaller and generally enriched with barium, Fe-oxides, phloids, and organic carbon. In addition, compared to the total clay fraction in the reconstructed pedon, the mobile colloids are more dilute in quartz and HF (hydroxy fluorapatite-variolites). Based on the results from scanning electron microscope (SEM) and photon-correlation spectroscopy, essentially all the mobile colloids (>90 %) have diameters of about 0.15 μm and moved through the soil as discrete and aggregated particles. They concluded the particles enriched with mobile colloids are not only readily-dispersible but also smaller in size than water-dispersible clay. Further, they proposed colloid mobilization in the pedon is a result of two consecutive processes: dispersion of highly charged particles due to changes in soil

density and reduced water flow, which is determined by particle composition and can be evaluated by water dispersibility of a soil, and their transport through a profile, which is non-dependent. However, it has to be realized that water dispersibility of soil particles obtained from a batch experiment is not always equivalent to soil's ability to stay detached (mobilized) in a soil. Colloid resistance time has to be taken into account, which has been discussed above and is supported by Kaplan (1994).

Influences of exchangeable cations percentage (CEC) on mobility of water-dispersible clay and colloids from soil colloids

Kaplan (1994) considered if particle size may or not a limiting factor for colloid release, the dispersibility of soil water-dispersible clay may correlate to colloid transportability in soils. The dispersibility of water-dispersible clay has been studied extensively (Johler et al., 1986; Sumner et al., 1993). Even though we cannot completely understand the dispersibility of soil colloids, it is undoubtedly affected by factors such as pH, cation strength and exchangeable cations percentage.

Kaplan et al. (1997) reported that colloid concentrations in the effluents from soil pores are highly correlated to the CEC of clay soils ($R^2=0.91-0.95$, pg. 8-9), but not to the soil pH or used electrolyte concentrations. They explained the dispersive property of the highly hydrated Na^+ ion structure as the positive correlation as the dispersion of the soil colloids appears to be a more important process in colloid release in the sandy soils. In fact, the positive correlation between soil colloid dispersibility and exchangeable cations percentage has been found by other researchers (Frankie et al., 1978; Sumner, 1984) who investigated the effects of arginine or methyl ox/hydroxide conductivity in a sandy soil.

Isa and Karadas (1997) examined the relation between the stability and transportability of water-dispersible soil colloids by pumping water-dispersible clay through an intact soil column. They found colloid recovery, after five pore volumes, depends on not only the type of soil column but also the characteristics of colloids. Among the colloid properties, pH and total exchangeable bases are significantly correlated with colloid recovery. The effect of pH on colloid migration can be explained by its effect on colloid stability: the higher the pH above the pH_c (> 4.0), the greater the colloid stability. The strong correlation between total exchangeable bases and colloid recovery is unexpected because of its high correlation with pH. In addition, they stated "correlation of total exchangeable bases to colloid transport may derive from cation-exchange reactions between the colloid-saturating cations and the column cations, which reduces colloid interaction with matrix surfaces and thus enhances colloid transport". Finally, they concluded the best single independent variable predicting colloid recovery is total exchangeable bases ($R^2=0.47$).

Even though there is some inconsistency among the results in different studies described above, there is sufficient information to show ESP is consistently correlated to the dispersibility of soil colloids in a soil. Rengwanz (1962), however, demonstrated that even Ca-saturated clay, i.e., ESP=0, could be dispersed provided the soil is free from electrolyte by dialysis, suggesting exchangeable Na is not essential for dispersing a soil. Further, in a soil system, where chemistry is dynamic and, therefore, concentrations and types of cations in soil columns and exchange water may vary greatly. In this sense, parameters such as total exchangeable bases, which reflect cations besides sodium from sodium, may be more reasonable to describe colloid transportability. The effects of

ion-exchange reactions in colloidal systems have been demonstrated by Ray et al. (1986) which will be discussed in the following section.

Ion transport processes during colloidal release

Observation of ion transport during colloidal release in well-defined systems Kelley et al. (1984) examined the effects of several electrolytes on the detachment of spherul colloidal particles of polystyrene from glass surfaces in laser media. They unexpectedly found colloidal removal was enhanced with increasing concentration of NaClO_4 . Such unusual behavior could be predicted if constant potential is assumed. They explained this behavior accordingly as a double layer that undergoes relaxation during particle detachment. In order to keep the potential constant at the distance between the particle and the surface increases, the absorption of the potential determining ion (ClO_4^-) must occur with subsequent equilibration of all ions (anions in the fixed and diffuse layers). During particle detachment, ion transport from solution phase into the ionothermal layer is accelerated with increasing distance between the surfaces due to relative influx from bulk. Kelley et al. (1987) summarized the unusual behavior can be observed under the following conditions, colloidal suspension is neutral (pH=7), particles and media have same charges, surface potentials are constant during colloidal detachment. They argued this apparently unusual behavior can be understood if one takes into consideration the energy profile near a surface of distance near the surface (Figure 3-1). The probability of colloidal detachment depends on the depth of energy well ($E_{\text{max}}-E_{\text{min}}$) which is a function of several parameters. On the other hand, the probability of colloidal deposition depends on the height of the energy maximum (E_{max}). As the concentration of

NaNO_3 , as the system increases, the depth of energy well reduces, resulting in an increased rate of colloid detachment, at the same time, the energy maximum decreases, resulting in an increased rate of deposition. The amount of colloidal particles observed in effluents is determined by the nature of these two opposite processes.

The nature of Kolbys (1984, 1987) indicates is that a change in the electrical environment of the surface, resulting from colloid detachment, may induce ion flow between solution and surface (EDC), which in turn may facilitate colloid detachment. This has been known as so-called surface charge- or potential regulation, which has been discussed by Chen et al. (1979). They have shown there may be significant ion flow between solution and interface during EDC interaction of the particles carry pH dependent charge. This includes ion transfer (H^+) may also be important during colloid release since pH-dependent charge is generally observed on soil colloid particles.

Soil structure, clayey soil, colloid, multivalent anions

Stenberg et al. (1984) examined the effects of electrolyte concentration on hydraulic conductivity (HC) of a silt soil. One of the major mechanisms of the influence of electrolyte concentrations on hydraulic conductivity is by modifying soil colloids and thus plugging their pore conducting paths. They found both clay dispersibility and hydraulic conductivity of the soil were very sensitive to the level of exchangeable Na in the soil and to the salt concentration of the precipitating solution. When salt concentration in the soil solution was 3.8 meq/liter, clay dispersant increased and HC decreased only if ESP > 115%. Conversely, when salt concentration was reduced to 0.3 meq/liter, clay dispersant increased and HC decreased when ESP > 16.2%. These results indicate that ESP itself can not decrease soil dispersibility, and salt

concentrations in solution have to be taken into account. A simple principle behind this is colloidal flocculation when the critical flocculation concentration of a salt is reached. The higher the IEP of the clay and the lower the salt concentration in solution, the higher the tendency for a salt to disperse, and consequently the IEC decreases. Further, they evaluated the response of soils to low IEP and leaching with low electrolyte water depends on the concentration of electrolytes in the soil solution that the total phores of each soil maintains (Shainberg et al., 1981b). They demonstrated soil concentration in solution was determined by the desorption rate of soil minerals, and higher cationic dilution was resulted in low aspect of exchangeable Na on soil dispersion. Obviously, soil dispersion results from equilibrium of colloid deposition and release. However, it is clear that the connection between cationic ion-exchange rates and bulk solution significantly impacts colloid mobilization.

There is sufficient evidence exchangeable Na has significant influence on colloid release from soil when it is exposed to an influent with low ionic strength. Cussner and Kelley (1971) first demonstrated the hydrolysis of exchangeable Na^+ in soil, or the replacement of exchangeable Na^+ by H^+ from the dissociation of water. They found, in the absence of CaCO_3 and CO_2 , a Na-saturated soil leached with distilled water yields a NaOH solution. In an experiment with Na-montmorillonite, where the hydrolysis products are removed continuously, Bar-on and Shainberg (1976) found a Na^+ concentration of 2×10^{-3} in the effluent. Shainberg (1971) demonstrated Na-montmorillonite releases Na^+ ions when the reaction products are not removed. He found the specific conductance of the clay dispersion is proportional to the square root of time. These observations are consistent with a hydrolysis mechanism consisting of two

convective resistance, a rapid exchange between exchangeable Na^+ and H^+ , which results in an acidic surface, a slower, fast-order transformation of H clay to Mg or Al clay, which increases the amount of exchangeable Na^+ release. In soils, similar phenomena have been observed. Omer and Staehelin (1979) demonstrated that, washing three soil-suspensions with de-ionized water, the release of electrolytes can be related to the uptake rate of ions exhibiting two linear rates in time sequence. They concluded that the first rate (the most rapid of the two) which occurred right after the washing (0.1–0.5 h), depends on exchangeable Na. Increasing ESP causes increases in the release rate of electrolytes.

In general, the flux of each ion species i across the boundary of the EDL around a particle is governed by the convective-diffusion equation (Van der Ven, 1980):

$$N_i = -u_i n_i / F + D_i \nabla n_i / n_i + v_i \quad (2.7)$$

Where N_i , u_i , v_i , D_i and ∇ are the flux of ion species i , electric field acting on i , concentration gradient of ion species i from bulk solution to interface and the bulk velocity of the fluid medium, respectively. They are all vector quantities. n_i , F , n_i , D_i and D_i are the charge per mole, valency, diffusion coefficient, and bulk concentration, respectively, of ion species i . Once a colloidal particle starts to detach from an electrified surface in a quiescent system, the electric field acting on i in the surrounding EDL, will change (∇ ($\nabla n_i / n_i$)) as the result of colloid detachment, resulting in changes in N_i because u_i and v_i do not change much during colloid detachment under stagnant flow during a very short period. With this in mind, the experimental observations we just discussed above can be understood conceptually. Once the electric field acting on a colloid decreases during colloid detachment, exchangeable Na is more readily able to diffuse to bulk solution compared to Ca^{2+} , Mg^{2+} , K^+ and etc. This has been confirmed by

the fact that electrolyte concentration in solution increases much faster at higher CaCl_2 for a soil (Kumar et al., 1975). It is known that a greater amount of ECE, represents, which results in increase in repulsive forces between soil colloids or colloids and pore media, and thus mobilization of soil colloids. Therefore, it is easy to understand the observation that colloid mobility are proportional to ECE (Kaplan, 1994) as well as total exchangeable cations (Sera et al., 1997). This is consistent with the study by Roy et al. (1990), which is based on cation exchange reactions.

Isolation of clayey soil colloids from a soil column

We have examined here colloid mobility in a Fe-contaminated soil, collected from Industrial Coochib, is affected by water-flooding conditions (Chapter 3). The soil packed in a series of short columns was incubated for approximately 3, 20, and 40 d, respectively. After the standing water on the top of soil columns was removed, 0.01 M CaCl_2 solution was pumped through the soil columns and the soil was treated with CaCl_2 . This is frequently observed the effluent resulting from column packing and to use Ca as an eluent for the transfer of clay colloids release. The effluent was then removed from CaCl_2 as deionized distilled water (DDW) and effluent of ~10 L soil was continuously collected using a fraction collector. Total soil dissolved metal concentrations were analyzed. The relation among colloidal Al, Fe, dissolved Ca, and pH with pore volumes of the effluent is presented in Figure 1-2 to demonstrate the proposed mechanisms for Ca release.

After saturating the soil columns with 0.01 CaCl_2 solution, Ca was the dominant cation in both bulk solution and aqueous double layers surrounding colloidal particles or stationary solid phases in the soil. When the effluent is collected from 0.01 M CaCl_2

relation to EDT, the release of Ca from the soil is determined by various mechanisms, which must likely occur to play sequentially. Firstly, at the beginning stage of washing to EDT, Ca release is from the bulk solution, which is confirmed by the fact that Ca concentrations and pH in the effluent at pore volumes <1 are approximately those of the influent ($[Ca] \sim 2.8$ [g], pH=6.95) (Figure 3-3). Secondly, Ca diffusion from EDT to the bulk solution driven by a concentration gradient occurred from two to 11 pore volumes. When Ca in the bulk solution was depleted, Ca starts moved against electrostatic attraction away from the surface, expanding EDT surrounding colloids and solid phases to mobilize colloids. Obviously, any significant expanding of EDT and washing colloidal mobilization has to be associated with significant amount of Ca released into bulk solution. In this case, the source Ca^{2+} in the diluted bulk solution may be associated with hydrolysis of release product ($Ca^{2+} + H_2O \rightleftharpoons CaOH^+ + H^+$) (Glover et al., 1979), resulting in a decrease in pH, which is consistent with our data (Figure 3-3) and consistent with the mechanism we proposed above. Generally, Ca hydrolysis is weak in solution and, thus, not likely to bring the pH down as low as we will as shown in Figure 3-3. In a heterogeneous system such as this case, however, deficiency of negative charge existed in the bulk solution, hence it is possible that the charge deficiency may further drive Ca hydrolysis. Thirdly, Ca desorption from colloidal surfaces and stationary solid phases occurred from 11 to 23 pore volumes (Figure 3-3). That are slow process and gradual, appeared at high pore volumes, resulting in no increase in repulsive forces between colloids and stationary solid phases. Increases in Ca concentrations and pH were observed in the effluent at pore volumes 17-23 (Figure 3-3). In essence, this process is equivalent to solubil Ca displaced by H^+ . However, a direct evidence is needed.

Nevertheless, this could be a moderate illustration for ion transfer between EDAs and bulk solution as described by Eq(2-7). Significance for transfer (C_a and C_{b0}) during colloid release provides a more promising approach to evaluate colloid mobility in a well mixed medium colloid theory for fixed release difficulty in soils because of its heterogeneity in both structure and composition of soil particle surfaces.

Association of Colloids with Heavy Metals

There are two major issues involved here: sorption capacity of heavy metals in soil colloidal particles, which has been well documented (Haque et al., 1999; Dzombak, et al., 1990), and will be briefly described in the following section, and influences of metal sorption on colloid mobility. The association of colloids with heavy metals can be classified into adsorption, precipitation (surface precipitation) and ion exchange. Their reflection on surface charge are possibly by virtue of heavy metal ions functioning as specific adsorbing, potential determining, and indifferent ions, respectively. Since most heavy metals are less in solubility in soils and their concentrations are much lower than those of electrolytes in soil solutions, it is not for them to function as indifferent ions. The same reasoning may also apply to the role of heavy metal ions play in potential determining ions. However, it has been realized that adsorption is one of the most important mechanisms of heavy metal association with colloids (Haque et al., 1999) and colloid facilitated heavy metal transport (Kotocshansk et al., 1987), which will be discussed next.

In soils, colloids are heterogeneous, including weathered minerals (clay mineral cations: Fe^{2+} , $CaCO_3$, silica, large organic molecules and sulfate esters). However, they

may be classified based on surface functional groups: surface hydroxyl, carboxyl, carboxylic anhydride group, etc. As an example, we will discuss hydroxyl surfaces in detail.

Adsorption of heavy metals on surfaces with surface hydroxyl

Surface-hydroxyl-bearing minerals are abundant in soil, such as metal oxides, quartz, and the edge of kaolinite. Similar with the expressions for the de- and protonation processes described previously, surface complexation reactions of surface hydroxyl with heavy metals can be written as follows (Hiemen et al., 1987):



Where SOH denotes a surface site and M^{n+} represents a metal cation. $K_{1,\text{app}}$ and $K_{2,\text{app}}$ are the apparent surface equilibrium constants and defined as

$$K_{1,\text{app}} = [\text{SOH}]^{n-1} [\text{H}^+] / [\text{SOM}] [\text{M}^{n+}] \quad (2-8)$$

$$K_{2,\text{app}} = [\text{SO}]^2 \text{M}^{(n-2)+} [\text{H}^+]^2 / [\text{SOH}]^2 [\text{M}^{n+}] \quad (2-9)$$

where $[\]$ indicates concentrations. Because of the charge characteristics of solid surfaces, ion activity at the surface needs to be corrected to obtain the intrinsic equilibrium constants. Accordingly, the intrinsic equilibrium constants can be expressed as

$$K_1 = K_{1,\text{app}} \exp[\alpha - (F\psi/RT)] \quad (2-10)$$

$$K_2 = K_{2,\text{app}} \exp[\alpha - 2(F\psi/RT)] \quad (2-11)$$

where α is the potential difference between the binding site and bulk solution. The exponential term accounts for the coulombic contribution to the intrinsic equilibrium constants. Because the surface potential cannot be determined experimentally, it is generally formulated based on a variety of models, such as constant capacitance, diffuse layer and triple layer models. It has been found that these models are equivalent in

preparing metal-adsorption on surfaces. Applying mass and charge conservation, then to combine this and correcting for the induction effect from the charged surface, the constant equilibrium constant for metal ions-binding to surface can be determined, however, it is somewhat model-dependent.

It has been found stability constant of surface complexes correlate with those of the hydroxide complexes in aqueous phases (Schindler et al. 1987). This could be supporting evidence for Eqs (1-8) to (2-17), which assume a surface complex is an analogous to aqueous complex and then Gibbs free energy of adsorption is the sum of enthalpic and enthalpic terms. Recently, Zhou (1998, 1999) pointed out the importance of ion hydrolysis during adsorption, and Dzombak (1991) has divided the adsorption term into a solvation contribution and a remaining term. Thus the overall free energy of adsorption of an ion can be written as

$$\Delta G_{\text{ads}} = \Delta G_1 + \Delta G_2 + \Delta G_{\text{resid}} \quad (2-18)$$

In this equation, the induction term (ΔG_{resid}) represents its contribution to the overall free energy of adsorption owing to the interaction between the ion and surface charge, the solvation term (ΔG_1) accounts for the role of solvation during adsorption of the ion, and the remaining term, named adsorption constant term (ΔG_2) is assumed to be a property of the ion alone. With this approach, the experimental results for Pb^{2+} , Cd^{2+} , Cu^{2+} , Mg^{2+} and Ca^{2+} can be closely reproduced (Dzombak, 1991).

If ligands other than H_2O and OH^- exist in solution, such as Lewis acids or bases (after the ion is adsorbed), competition may occur among dissolved ligands, heavy metals and surface adsorption sites. The competing species (e.g., sulfate, phosphate or dissolved organic carbon (DOC)-carried) surface complex, and formation of aqueous metal-DOC

complexes reduces the metal ion release and effectively decreases the amount of aqueous metal ions available for adsorption. In addition, anions such as sulfate and phosphate will combine with metal cations, reducing the metal adsorption available. On the other hand, metal sorption may be enhanced by the formation of strong surface complexes via sulfate and phosphate and DOC. At the present time, there is no theory that can describe these complicated processes well. However, in principle, the partition of any aqueous species may be described under the framework of Debye-Hückel theory (199; Sverjensky, 1991).

In metal metal systems, heavy metal ions interact with surfaces in specific adsorbed ions (Lippmann, 1984; Aylward, 1983) as their charge development, which is similar with the situation described previously.

Effects of heavy metal adsorption on the chemistry of soil colloids

A number of studies have indicated the importance of particle adsorption

in determining surface properties of colloids in natural waters. Electrokinetic measurements made on natural particles dispersed in sea water and natural fresh waters have shown that their electrokinetic mobilities tend to fall within very limited ranges of negative values. The apparent uniformity of this surface electrical property has been attributed to the adsorption of organic materials, particularly humic compounds, at the particle surfaces, which has been supported by a number of studies using synthetic systems. It has been shown that the effects of adsorbed organic compounds on surface properties of mineral particles in natural waters are modified, to some extent, by additional cationic constituents. In this sense, the interactions of heavy metals with the surfaces of soil colloids cannot be described by the interaction between heavy metals

and pure minerals, rather by those between heavy metal and the complementary surfaces of "real" soil colloids. This complement includes the complexity of colloid shapes and three-dimensional interfaces between solution and colloids. One of most important examples is organic-coated oxides. It has been proposed as a model individual colloid particles: newly formed of amorphous oxides coated with sorbed Fe_2O_3 & like (hydroxy)oxides and/or organic matter (Kohn (Day et al. 1994) which generally possesses similar composition with soil colloids as well as three dimensional interfaces.

There has been a fair amount of research done dealing with how metal strength at pH affects the mobility of the colloids with the constituent components alone (Day et al., 1994). However, little is known about the effects of heavy metals on colloidal charge development and stability of the complex colloids. Only recently, Karamanlian et al. (1992) have implicitly taken into account the effects of absorption of Pb^{2+} and Cu^{2+} onto humic-coated oxide colloids on colloid charge development and transportability. They investigated the influence of adsorbed heavy metals (Cu^{2+} and Pb^{2+}) on the transport and deposition location of fulviculic acid humate, coated with humic acid suspended in Ca^{2+} solution, through a natural soil. They found that replacement of Ca^{2+} by Pb^{2+} while holding the total concentration ($\text{Ca}^{2+} + \text{Pb}^{2+}$) fixed resulted in a slight decrease in electrophoretic mobility of humic-coated humate colloids. When Ca^{2+} was completely replaced by Pb^{2+} , the suspensions were destabilized and aggregated within 20 h. In contrast, replacement of Ca^{2+} by Cu^{2+} had very little effect on electrophoretic mobility and colloidal stability. Both Pb^{2+} and Cu^{2+} are known to bind much more strongly to humic substances and Fe oxide surfaces than Ca^{2+} . At the pH of the suspensions investigated (pH 5.0), Cu^{2+} has a higher affinity for humic substances than Pb^{2+} , but Pb^{2+}

adsorb more strongly to humate than Cu^{2+} . In fact, the interface is three-dimensional since the humic coating can be considered as an ensemble of humate particles in the solution phase. The binding-differences may derive Pb^{2+} and Cu^{2+} to bind preferentially at S and O diffuse layers, respectively. Therefore, it is expected that the effect is more pronounced by replacing Cu^{2+} with Pb^{2+} than with Pb^{2+} in the colloid suspensions on electrophoretic mobility and colloid deposition. Their results suggested that humic-coated oxide colloids can be stable and mobile in the presence of strongly adsorbing trace metals.

Enhancement of heavy metals in soil colloids

The ability of colloids to facilitate heavy metal transport is largely determined by the distribution of heavy metals among solution, mobile colloids, and stationary phases. Mills et al. (1994) first incorporated partition coefficients into their model in describing colloid-facilitated metal transport in porous media. However, a mechanism concerning the distribution of metal distribution among different phases is still missing. One of the major reasons is the dynamic features of the distribution of heavy metals, and phase transformations among them, make it from mobile to immobile colloids, mobile heavy metals are introduced to a system. Kuylen et al. (1993) have found that the sorption of mobile colloids from contaminated soils is significantly different from that from the uncontaminated soil or not soil, suggesting the association with heavy metals may alter greatly the mobility of organic mobile colloids.

Anderson et al. (1991) measured the potential of colloid-facilitated heavy metals in mobile soils receiving during rain. There are two during regime considered: NaCl and calcium magnesium acetate (CMA). In their experiments, a series of 10 soil samples

were packed with 30 g of soil. The columns were leached on a constant vacuum extractor with three consecutive 30-ml. aliquots of either 0.1 mol l^{-1} NaCl or CH_3A . After initial leaching with either of the soils, the columns were leached with three consecutive 30-ml. aliquots of deionized water. This is to simulate the input of only runoff water to the residue soil, followed by groundwater or rainfall. A portion of each leachate was saved without any further filtration and the remainder of each solution was filtered through a 0.45 μm membrane filter. Then the filtrates were immediately placed into a stored sterilization cell with a membrane of 0.005 μm PTFE. This procedure separates the particles into three fractions: >0.45 μm , between 0.45 μm and 0.005 μm and <0.005 μm . The results have shown that the residues leached particles, through the whole process, vary with the initial soil input. In general, NaCl tends to mobilize soil colloids more than CH_3A (Anderson et al., 1993). On the other hand, because of the possibility of artifacts resulting from column packing in their study, it may be more reasonable to examine the leached cumulative particle including the first several pore volumes. Figure 3-3 is a plot of leached cumulative particle after switching the elution from soil solution to deionized water. It is well established that reduction of ionic strength may mobilize soil colloids. As shown in Figure 3-2, the concentrations of each metal (Ca , Pb , Pd , Ni

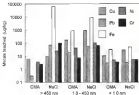


Figure 3-3 Cumulative concentrations of metals leached from the soil at the three size fractions after washing soil columns to deionized water. Size separation was by 0.45 µm membrane filter and 1-µm cellulose ultrafilters (membrane prepared from Amicon et al., 1990).

and Cr) are consistently higher in the fractions from wet columns pre-leached with NaCl than that with CMA in all three wet fractions. The fraction <1 nm will hereafter not be emphasized since it is generally considered as dissolved. Among these size fractions, colloids ranged from 1–400 nm is most important for colloid transport (Cupris *et al.*, 1995) and their concentrations of each metal are much higher for the columns pre-leached with NaCl than those with CMA. This is consistent with current notions, that is, the presence colloid mobility and to some colloid-facilitated metal transport of one assumes accumulation of metals with sub-fractions are not significantly affected by changes in solution chemistry. Furthermore, metals in fractions > 400 nm are much higher than those in fractions < 400 nm for columns pre-leached with CMA, whereas there are no significant differences for the columns with NaCl except for Fe and Cu. This suggests CMA is more selective in mobilizing smaller colloidal particles than NaCl. Along with this fact, the column pointed out that colloidal Cu did not correlate with with DOC between the two fractions for the columns pre-leached with NaCl, nor does colloidal Fe with other colloidal metals pre-leached with CMA (Figure 3-2). This suggests that heavy-metal-bearing organic colloids vary with both wet and solution chemistry. In other words, phase transformations among heavy-metal-bearing colloids, such as metallic insoluble colloids or organo-metallic colloids with various sizes, has to be taken into consideration.

We have examined the effects of water flooding leaching on colloidal Pb mobility in wet columns. Detailed descriptions about the experimental procedure can be found in Chapter 5. As shown in Figure 4-3, colloidal Pb concentrations are varied with wetness. Interestingly, there was no significant difference in concentrations <1

colloidal Fe and Al for the first several pore volumes when the columns were acidulated from 3 to 20 d, while concentrations of colloidal Fe decreased approximately 8 times after 20 d than 3-d acidulation. This suggested that Fe-bearing colloids tended to be immobilized or the tendency of association of Fe with mobile colloids decreased with water (pore) residence.

Concluding Remarks

Soil has structurally different features at colloid mobility-compared with well-defined porous media or subsurface systems. At the present time, it is not realistic to predict colloid mobility and colloid-facilitated heavy metal mobility in soil with certainty.

Soil colloids are exposed to solutions when they take part in chemical processes. Therefore it is difficult to predict charge development of soil colloids since it is determined by the interaction of surfaces and solutions. Point of zero charge (PZC) of mineral particles suspended in simple solutions can be theoretically predicted, while little information has been obtained in soil. In general, soil particles are assemblages of crystalline and amorphous minerals, and organic materials; for such particles sophisticated models such as triple layer model do not make much sense in describing the identified interfaces since particle surfaces are irregular and the Stern layer is often inside of the physical boundary of the particles. As a first approximation, however, it may be more practical to describe soil particle interfaces by diffuse double layer with a specific part (a charged surface), and a generic part (a diffuse layer). The surface charge development process may be described by the protruding of charged species between solution and surfaces assuming the charged species are mobile between the two phases. Similarly, the association of heavy metals with colloids may have significant influences on colloid

mobility, which is subject to changes in dynamic solution chemistry. However, any localized release is as available at the present time.

Colloids are ubiquitous in soils. Colloids from clayey parent material, the surfaces of soil colloidal phases consist of deposited colloids. Consequently, the blocking effect of colloid deposition in soil is obvious, which may greatly enhance colloid mobility in soil compared to that in a noncolloidal clayey parent material. Under such a condition, soil structure is a dominant mechanism in soil colloid deposition. The deposited-colloids may release depending on the nature of interaction with the necessary phase, that is, the interaction energy profile (Figure 3-1), which vary because of heterogeneity of the surface. Phenomenally, this process is time-dependent or condition-dependent, and therefore, is referred to as transient phenomena in colloid deposition. At the present time, wheat straw-derived clay extracted from a soil is widely used to indicate colloid mobility. However, it has to be realized that in both cases there are two mechanisms, opposite processes, colloid deposition and release. In a given system, the relative effect of each on either soil clay dispersion or batch-scale or colloid mobility in a column experiment depends on mobile-colloid residence time in the system.

Despite the shortcomings of the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory, we believe it provides a basic theoretical framework in describing soil colloid deposition and colloid deposition and release, which is simple and applicable in concept. It has to be pointed out that all modern colloid theories (not only the DLVO theory) are difficult to apply to soil because of its heterogeneity in both structure and composition of soil particle surfaces. In order to discuss the potential mobility of soil colloids, a phenomenological approach may be more practical. Soil colloids possess high

concentrations of exchangeable ions in the PDLs (high Cl^-), which does not always equilibrate with those in bulk solution. It has long been recognized that cell-sol activity is not so coupled by significant ion transfer between PDLs and bulk solution. By evaluating the possibility of the ion transfer, potential cell-sol activity may be estimated qualitatively.

CHAPTER 3 RELATION OF Pb SOLUBILITY TO Pb PARTITIONING IN SOILS

Introduction

Lead contamination is a source of environmental degradation due to its toxicity to both humans and animals (Ma et al., 1993). In general, Pb mobility is low because of its low solubility. Lead solubility may be further reduced as a result of its interaction with soil solid phase via sorption and ion exchange. However, enhanced Pb solubility has been found under both laboratory and field conditions (Amthor, et al., 1994; Chemsakyan, 1994). As such, Pb may migrate through a soil profile to contaminate groundwater.

Although much effort has been spent to model heavy metal solubility (Coulthart et al., 1983; Sposito, 1984), such prediction under field conditions involves large uncertainty. It is partially because of the difficulty in assessing the effects of dynamic soil solution chemistry on heavy metal speciation. However, changes in solution chemistry such as pH, redox potential and ionic strength may shift Pb chemical processes significantly. These aspects may be further complicated by aqueous Pb competition with other cations for ligands, which may enhance Pb mobility under certain conditions (Amthor, et al., 1994).

In natural aquatic environments, $Pb(II)$ and $Pb_2(II)$ have similar affinity to complex with ligands, and thus they show similar patterns of species distribution (Turner et al., 1981). Theoretically, both $Pb(II)$ and $Pb_2(II)$ are in "transient state" in terms of

acid distribution) based on electronegativity and covalent radii (Walton and Richardson, 1980). This evidence implies that it is important to examine Pb chemistry when studying Pb solubility. In fact, good correlation ($r^2 = 0.71$, $p < 0.05$) between concentrations of aqueous Pb and Fe in sediments has been reported (Lee et al., 1993; South and Benoit-Nelson, 1994). In soil environments, data published by Karamanidis (1994) showed that concentrations of mobile Pb and Fe were related ($r^2 = 0.34$, $p < 0.05$) in several polluted soils near a copper smelter. The theoretical evidence along with the published experimental data suggests that Pb and Fe solubility may be related in a soil.

In addition, there are two other possible factors for correlation between Pb and Fe in solution. First, Fe (oxy)hydroxides are good sorbents for aqueous Pb (Adams et al., 1994; Loefer, 1985; Benjamin and Loefer, 1991), and their distribution as precipitates may reflect as such Pb. In soils, dissolution of Fe (oxy) hydroxides is generally promoted by reducing Fe (III) to Fe (II), which is sensitive to red-oxim status (Loefer, 1985; Goshi and Pardo, 1994). Under reducing conditions, Fe (oxy) hydroxides tend to mobilize Pb (Cambrell et al., 1989), whereas under oxidizing conditions they dissolve to release Pb (Cambrell, 1994). Secondly, soil organic carbon, especially dissolved organic C (DOC), is an important factor controlling Pb and Fe solubility in soil (Dow and Munnick, 1990; Davis, 1994; Loefer, 1985). DOC functions as a ligand to complex with Pb and Fe to increase their solubility (Davis and Loefer, 1983). On the other hand, DOC may also be coated by Fe (oxy) hydroxides under certain conditions, via ligand exchange or hydrophobic interaction to soils (Murphy and Janssen, 1993), thus decreasing Pb and Fe solubility.

Despite all the circumstantial evidence that Fe solubility impacts Fe solubility in soil, there has been little effort to quantify the relationship between the two. However, understanding the relationship between heavy metal solubility and the behavior of Fe may provide important information for assessing potential mobility of heavy metals in soil environments, which cannot be provided successfully at present time.

Soil redox status varies temporally The intensity of redox status can be described by redox potential *in general*. In surface soil it is influenced by rainfall, humidity, and changes in land use, whereas in redox zone by fluctuation in water table (Bhat et al., 1997). The redox potentials of sediments that contain reduced iron can be measured readily, whereas characterization of the redox status in a soil is still a challenge. As mentioned previously, however, soil redox status affects metal solubility greatly under certain conditions. To evaluate the effects of varying redox status, saturated/unsaturated (partial) saturated) incubation techniques have recently been developed (Marsden et al., 1994; Kuczworska, 1996). Water-flooded incubation of soil was used to effectively decrease soil redox potential to study the speciation and fate of heavy metals in contaminated soils (Kuczworska, 1996). Even though saturation rarely happens in surface soils, some valuable information may be obtained from such a study. In this paper, two redox sensors in soils will be observed under water flooding (saturated) and no flooding (partial) conditions.

The major objective of this chapter is to examine the relationship between Fe solubility and Fe partitioning in soils with different redox chemistry. Throughout this paper, Fe potential will be expressed as a concentration ratio of aqueous to solid Fe (C)

unless otherwise specified. The results showed that *Ph* solubility was related to the ratio in the soil.

Materials and Methods

Locations and characteristics of soil samples

The soil samples used for this study were collected in March 1996 from a research site in Manatee County, Florida. The soil is an underflow sand (fine-grained quartzarenaceous) with a specific horizon below 2 m. The samples were collected from 2–10 cm below the surface after removing surface residue. The samples were air-dried, sieved through 2-mm screen, and stored at 4°C prior to use. Some characteristics of the soil are listed in Table 3–4.

Column construction

A series of 10 soil columns (columns, 40 × 4 cm), which were prepacked with a layer of 3 mm of acid-washed Ottawa sand (20–30 mesh) at the bottom, were packed with 40 g of soil sample. The columns were then packed with another layer of the acid-washed sand on the top to minimize disturbance to the soil from influence. All the syringes were set on a Constant Volume Extractor (Constant International, Littleton, CO) for extraction and leaching. The extraction procedure was as follows:

Extracting soil solution. 10 mL of deionized distilled water (DDW) was slowly poured into each column and the soil solution was extracted for 48 h before the water was extracted.

Table 3.1 - Characteristics of the Florida soil used

pH	Organic C mg g ⁻¹	Extractable N ^a mg kg ⁻¹	Total concentrations ^{b,c}					Extract ^{***}		
			Ca	Fe	Li	Ni	Pb	Se	Si	Zn
5.8	6.8	81.9	3647	576	87	21	1.1	34.4	4.5	2.8

^aOlson et al., 1996^bIda et al., 1999^cDay, 1967

Addition of sorption Pb. 38 mL of 0.68 mg/L $Pb(NO_3)_2$ was added to 12 soil columns and 10 mL of 1.68 mg/L $Pb(NO_3)_2$ to 14 soil columns. The columns were extracted after 24 h at 2.5 mL h⁻¹. This resulted in lead-loading rates of 0.36 (low Pb loading) and 2.52 mg/kg h⁻¹ (high Pb loading) in two groups of soil columns.

Addition of electrolyte solutions. 38 mL of different electrolyte solutions was added to different columns to vary solution chemistry. DCPW of pH 3.3 and 2.17 and 4.34 mg/L NaCl solutions were added to the first 12 soil columns, and 0.10, 1.08, and 2.12 mg/L NaCl solutions, 0.79, 0.85, and 1.18 mg/L $CaCl_2$ solutions, and DCPW of pH 4.3 and 3.3 to the other 14 soil columns. The columns were extracted next after 24 h at the rate of 2.5 mL h⁻¹. For the first 12 soil columns with low Pb loading, each treatment was replicated four times (three treatments) and for the 14 soil columns with high Pb loading, each treatment was triplicated (six treatments). Soil columns in each treatment (a total of nine treatments) varied not only in Pb concentration but also in pH and composition of leachate solutions.

Isolation of soil columns. The above 28 soil columns (with the same Pb loading rate and electrolyte solution) were further divided into two subgroups (14 soil columns each) for incubation. One subgroup was filled with 30 mL of DCPW (2 cm above the soil surface) for water flooded incubation. The other subgroup was incubated as it is for non-water flooded incubation. All soil columns were incubated for 42 d at room temperature.

Leaching. DCPW was added to each soil column to make 30 mL of leaching water above the soil for all columns before leaching. The leaching was conducted at 60 mL h⁻¹ and approximately 15–60 mL leachates were collected. The soil samples with moisture content > 15% in the columns were sealed and stored in refrigerator for further analysis.

Leachate collection and analysis

Separation and analysis were applied for both leachates and leached soil samples to investigate the relationship between Pb solubility and Pb partitioning in the soil. The pH was measured immediately after the leachates were collected. The leachates were then filtered through 0.22 µm membrane filters. The filtrate was analysed for DOC and total Pb and Fe concentrations. The filters and columns were removed in water meant to push the soil out of the syringe with minimum disturbance. The extract soils from the columns were then divided into three equal sections (top, middle and bottom) for further analysis. The data presented in this paper for soil, however, was the average over the three sections since there were no significant differences in Pb concentrations in the three sections. Fe(III) content in the leached soil was analysed following the same method described in Chapter 3.

Result and Discussion

Pb solubility

Aqueous Pb concentrations in leachates showed strong pH-dependence with $r^2 = 0.92$ for soils with Pb loading of 1.90 mol kg^{-1} (high Pb loading, Figure 3-1 A). Aqueous Pb concentrations decreased as pH increased from 4 to 6. It has long been recognized that pH is an important factor affecting metal solubility, with aqueous metal concentrations increasing as pH decreases (Chen et al., 1996). Leachate Pb concentrations in soils with Pb loading of 0.26 mol kg^{-1} (low Pb loading) were also correlated with pH with correlation coefficient of $r^2 = 0.21$ ($p = 0.005$). However, they

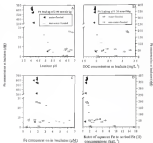


Figure 3-1: Relation between Pb solubility and leachate pH, dissolved organic carbon (DOC), leachate Pb concentration, and ratio of aqueous Pb to sorbed Pb (R) concentrations in steady-state. Data from 2 90-minute 10^{-3} Pb loading rate read from left y-axis and data from 0.36 minute 10^{-3} Pb loading rate read from right y-axis.

increased as pH increased from 8.1 to 9.5 (Figure 3-1A). Obviously, mechanisms that determined aqueous Pb concentrations in soils affect Pb leaching was different from that of high Pb leaching. It seemed that DOC was a primary factor in determining Pb concentrations in soils with low Pb leaching, as reflected by their correlation coefficient of $r^2 = 0.41$, $p < 0.01$ (Figure 3-1B), i.e. Pb concentrations increased as DOC concentrations increased. However, such correlation did not exist for soils with high Pb leaching ($r^2 = 0.26$), possibly due to the fact that Pb solubility was more strongly controlled by pH.

Beside pH, redox status is another factor affecting metal solubility in soil (Chen et al., 1996). Hunter (1984) suggested that it is reasonable to measure important redox systems instead of redox potential to indicate redox status in natural systems. We used aqueous Fe as a measure of redox status for soils. As expected, aqueous Fe concentrations were much higher in soils under water-flooded conditions than non-water-flooded conditions (Figure 3-1C). In soils with low Pb leaching, aqueous Fe concentrations was even three times greater under water-flooded conditions (average $2.12 \text{ } \mu\text{g/g}$) than under non-water-flooded incubation (average $0.57 \text{ } \mu\text{g/g}$). Similarly, the average aqueous Fe concentrations in soils with high Pb leaching were 4.46 and $1.74 \text{ } \mu\text{g/g}$, respectively. Greater aqueous Fe concentrations in soils with high Pb leaching than with low Pb leaching was mainly due to pH difference in the soils (Figure 3-1A). However, there was no relationship shown between aqueous concentrations of Fe and Pb for soils of either Pb leaching rates (Figure 3-1C). It was reported that aqueous Fe and Pb concentrations are linearly related due to the fact that heavy metals are released from Fe (oxy)hydroxide surfaces when it dissolves (Chen et al., 1996). In our study, however, this was not the case (Figure 3-1C), suggesting that aqueous Fe may not be controlled by

Fe (oxy)hydroxide surface sites. Similar results have also been reported by other researchers (Kinniburtt et al., 1990). These data suggested that, in general, aqueous Fe concentrations alone could not describe Fe solubility well. Nevertheless, as expected aqueous concentrations in soils under reduced conditions were much higher than those under less reduced conditions. Aqueous Fe concentrations in soils with high Fe loading were 32 times greater under water-flooded conditions (averaged $409 \mu\text{M}$) than under non-water-flooded conditions (averaged $12.4 \mu\text{M}$) (Figure 3-4). Similarly, aqueous Fe concentrations were 51 and 22 μM , respectively, for soils with low Fe loading.

Fe solubility and Fe partitioning

As discussed previously, pH was related to Fe solubility in our study. However, even for the same soils, the relation between pH and aqueous Fe differed with Fe loading rates (Figure 3-5A). In other words, there is no simple relation between pH and Fe solubility when soil redox chemistry varies greatly. There were no simple relationships between Fe and DOC concentrations and Fe and Fe concentrations either (Figure 3-5A,C).

To better describe Fe solubility, we defined the ratio of aqueous Fe to solid Fe (II) concentrations as a Fe partitioning index. In this study, solid Fe (II) was operationally defined as Fe(II) that was extracted by 0.1 M HCl (Lovley and Philp, 1987; Burns et al., 1990). By definition, Fe partitioning index represents the relative affinity of aqueous Fe to solid phases in a soil. A larger number indicates a lower Fe affinity to solid phases. There was no simple relationship that existed between aqueous Fe concentrations and Fe partitioning index (Figure 3-5D). For soils with low Fe loading

and incubated under water-flooded conditions, the relation between aqueous Pb and Pb partitioning index was approximately parallel. In general, aqueous Pb concentrations increased as the index decreased. However, as the index decreased below 2 kg L^{-1} , increases in Pb concentrations were substantiated (Figure 3.12). A similar trend was also observed for soils with high Pb loading and incubated under non-water-flooded conditions, i.e. substantiated increases in Pb concentrations were observed when the index was $< 2 \text{ kg L}^{-1}$. However, no enhanced Pb solubility was found in soils with low Pb loading and incubated under non-water-flooded conditions since the Pb index was $> 2 \text{ kg L}^{-1}$. However, for soils with high-Pb loading and not incubated under water-flooded conditions, extremely high Pb concentrations were observed since the Pb index was $< 1 \text{ kg L}^{-1}$. Obviously, compared to pH, ORP and Zn concentrations, a more consistent relation between aqueous Pb concentrations and the Pb partitioning index in soils was observed.

Pb is a pH-dependent process. Karickhoff equation (Karickhoff et al., 1983) has been successfully used to describe the adsorption behaviour of metal partitioning in natural aquatic systems (Fuller et al., 1996; Tasson et al., 1993; Babiarz et al., 1993). In our system, the Pb index in soils with both high ($2^{\text{nd}}-0.64$, $p=0.001$) and low ($2^{\text{nd}}-0.10$, $p=0.001$) Pb loading rates was correlated to pH. Thus, the Karickhoff equation can be applied in our system as follows:

$$\log(\text{Pb index}) = -\alpha \text{pH} - \log K_p + \log N_s \quad (3-4)$$

where α is adsorptional proton coefficient, K_p is Karickhoff partition coefficient and N_s the total number of exchangeable sites (Fuller et al., 1996; Babiarz et al., 1993).

Assume that the above equation is correct, then the Pb index is related to pH is additive, i.e. K_p and N_s . The number of exchangeable sites N_s in the equation for a given soil is

generally a constant. On the other hand, γ varies with metal species in solution and on surfaces and K_p does not vary much unless the adsorption density exceeds its maximum (Richard et al., 1983). Therefore, for a given system, the Fe index changes mainly with pH and γ . The relation between pH and the Fe index in the Karickhoff equation is as follows. For soils with high Pb loading, pH was inversely related to the Fe index as expected with $r^2=0.22$ (i.e., the index decreased as pH increased from 4.1 to 6.0). However, for soils with low Pb loading, pH was positively related to the Fe index with $r^2=0.41$, $p<0.05$ (Figure 3-4 A&B). The impact of γ on the index is unclear at the present time.

As shown in the Karickhoff equation (Eq. 7-1), the Fe index is a lumped parameter that presents the properties of both soil solution (pH and γ) and solid (K_p and N_d) that determine Pb partitioning. To evaluate the relationship between Fe index and other metal solubility, it is expected that the more Fe-like element with the more related solubility is to the Fe index. As mentioned previously, Pb(II) shows some similarity to Fe (II) in both metal classification and speciation behavior in aqueous systems (Tanner et al., 1980; Nriagu and Richard, 1980). Therefore, it is expected that aqueous Pb concentration is well related to the Fe index (Figure 3-1C).

Tanner et al. (1980) reported that in natural waters Pb (II) and Fe (II) exhibit some similarity, meaning that Fe (II) may be a major competitive cation to Pb(II) for ligands. Therefore, it is important to evaluate the competition between Fe (II) and Pb (II) for ligands. It should be pointed out that, in this chapter, we did not emphasize the competition between Fe (II) and Pb(II) for adsorption sites on solid phases. The reason is that some researchers have shown that the competition may be insignificant (Hou and

(Barnett-Imbrogno, 1980; Campbell and Shanon, 1982). In our study, soil solution chemistry varied in different soil columns. These variations may shift the competition, as the present note, it is difficult to fully evaluate these effects on metal solubility in the soil, especially when DOC is present. The Fe index presented in this paper, however, may serve as a simple measure of competing ability of Fe with Pb for ligands. At this stage it is more important to look at the conceptual nature of the index than the detailed mechanistic interpretation, which need to be explored further in future.

Assuming that Fe and Pb compete for ligands in a soil, then the following can be inferred. As Fe partition index increases, there is more aqueous Fe and/or less sorbed Fe, which means there is more competition for ligands from aqueous Fe in the soil and thus results in less aqueous Pb in the soil. On the other hand, as Fe partition index decreases, there is less aqueous Fe and/or more sorbed Fe, which means there is less competition for ligands from aqueous Fe and thus results in more aqueous Pb in the soil as shown in Figure 3-13.

In theory, there should be a maximum for the Fe index, i.e., the ratio of the minimum of aqueous Fe concentration to the maximum sorbed Fe concentration. If aqueous Fe concentration approaches zero, i.e., all aqueous Fe was transferred onto sorbed form, the Fe index is zero. As this happens, Pb decreases the ligand competition in the solution, so that enhanced Pb solubility would be expected. The overall trend shown in Figure 3-13 is well understood in principle. In reality, however, aqueous Fe concentrations cannot be zero. Therefore, the Fe index must be larger than zero. Theoretically, once soil the minimum of aqueous Fe concentration is greatly decreased by the solubility of Fe minerals and the maximum sorbed Fe concentration is sol-

dependent. Therefore, the Fe index is generally consistent in solution chemistry at a soil. Since it is impossible to accurately measure the maximum extract Fe concentrations in a soil, no attempt was made to evaluate the soil value of the maximum Fe index. In the soil we used from the definition. However, the maximum Fe index when enhanced Pb solubility occurred was approximately 2 kg L^{-1} in the soil studied, which was estimated from the relationship between Pb solubility and Fe index (Figure 3-12). As expected, the number did not vary much with the land-use conditions and Pb loadings (Figure 3-12). It has been noticed that Pb concentrations around soil solution will disappear even when the Fe index was $< 2 \text{ kg L}^{-1}$ (Figure 3-12), which is similar to the present data. Nevertheless, the significance between Pb solubility and Fe index was that significantly enhanced Pb solubility does not occur unless the Fe index was $< 2 \text{ kg L}^{-1}$ (Figure 3-12).

Indices of Pb solubility and Fe partitioning in published data

In this research, extract Fe was defined as the Fe (II) fraction extracted by 0.1 M HCl, which is supposed to extract exchangeable, some adsorbed and loosely precipitated Fe(II) (Jensen et al., 1994). In addition, however, such data are not always available. In order to investigate best the relation between Pb solubility and Fe partitioning index, we defined in this paper using available data in the literature, other extractions that may be equivalent to 0.1 M HCl have to be used. Two published data sets were used. In both data sets, the Fe index was calculated using the total extract Fe instead of Fe (II) since the quantity of the latter is unavailable. However, Fe index calculated from either total Fe or total Fe (II) should be consistent conceptually since Fe (II) is more mobile compared with Fe (III).

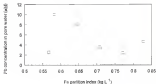


Figure 3-2 Relationship between Pt-concentrations in pore water and the ratio of aqueous and sorbed Pt (Pt partition index) in a contaminated sediment. Data are adapted from Lee et al. (1997).

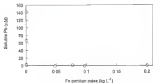


Figure 3.3 Relationship between soluble Pb concentrations and the ratio of soluble to sorbed Pb in naturalized soils. Data are adapted from Kocum-Özkan (1996).

The first data set was from Lee et al. (1997) who characterized a sediment contaminated by heavy metals co-contaminated with Pb. In the study, concentrations of aqueous Pb and Fe as a percentage of the sediment were analyzed, and Fe concentrations in the sediment was determined by sequentially extracting four fractions: exchangeable extracted by 1 M MgCl_2 , bound to carbonates by 1M sodium acetate bound to amorphous Fe and Mn hydroxides by 0.1M hydroxylamine hydrochloride and in 20% nitric acid bound to organic matter and sulfides by 20% H_2O_2 and 0.01 M nitric acid, and residual by concentrated HNO_3 and HClO_4 . Assuming that the sum of Fe concentrations in the first two fractions (exchangeable and bound to carbonates) was equivalent to that extracted by 0.5 M HCl , a plot of aqueous Pb concentrations to the Fe index/Pb concentration in pore water/the sum of Fe concentrations of exchangeable and bound to carbonates) is shown in Figure 3-2. A similar trend shown in Figure 3-1D was observed: enhanced Pb solubility occurred only when the Fe index was low. However, low Pb solubility was also observed at low Fe index as did in our data (Figure 3-1D). This again suggests that high Pb solubility will not occur unless the Fe index was below a certain value and low Fe index will not necessarily guarantee high Pb solubility.

The second data set was taken from Karamanli (1996) who determined concentrations of heavy metals via a sequential extraction as indicated by a copper constant. In the study, heavy metals were characterized via 7 fractions, i.e., soluble (1M NH_4NO_3), exchangeable (1 M NH_4OAc , bound to MnO_2 , 1M $\text{NH}_2\text{OH}\cdot\text{HCl}$ /1M NH_4OAc) and etc. We assumed that Fe extracted by 1M NH_4NO_3 is equivalent to the aqueous Pb concentration and sum of exchangeable Fe and bound to MnO_2 was equivalent to Fe(II) extracted by 0.5 M HCl . Again, a similar trend shown in Figure 3-1D was observed.

between soluble Pb and Pb uptake (Figure 3-13), i.e., highest Pb solubility was observed at the lowest Pb partition ratios and on the particular case the Pb index was zero. Like the data of Lee et al. (1997), the soil samples were collected from various locations (over a similar size in Poland and there were large variations in soil properties among the samples (C: 10–24 mg/kg⁻¹, organic C: 8.03–14.03%, clay content: 3–6.7%) (Kasprzak, 1998). This suggested that the relationship between Pb and Pb partition ratios may be applicable to field data even with large spatial variability in soil properties.

Implication of Soil Porosity

Partition coefficients (K_d) are important parameters in assessing the potential impacts from metal contaminated soils. However, K_d is not a constant in a dynamic soil environment. It is determined not only by the characteristics of solid phases but also solution chemistry. In a given soil system, variation in metal solubility (and hence K_d) is generally determined by metal solubility. There are several operation models available to describe the interactions of metals and soil components to predict their solubility. Unfortunately, such predictions generally lack accuracy primarily because of soil dynamic nature.

At the present time, measuring changes in solution chemistry in field conditions is difficult if not impossible. This information, however, is critical to estimate the solubility of heavy metals in operation models. In contrast, the approach presented in this chapter provides a simple relation between the probability of enhanced Pb solubility (or K_d) and Pb partition ratios, which is generally not sensitive to changes in solution chemistry. In this approach, we simply determine the maximum Pb index in a field condition to predict the possibility of enhanced Pb solubility (the lower K_d). Of course, more work is needed to

further test this concept, in different soils and determine the range of Fe under the enhanced Fe-availability.

Conclusions

Our data using a synthetically contaminated soil demonstrated that enhanced Fe-availability was only observed at low Fe partition ratios. Back-titration was also observed, using two published data sets as the literature, thus further reinforcing the relationship conceptually. Since data used in this paper were from various soil measurements (available evidence in Figure), Fe contaminated soil in Poland, a sandy soil from Florida, it is reasonable to conclude that Fe-availability may be indeed related to Fe partition ratios in soils. This concept may also be applied to availability of other heavy metals such as Cd, Cu, Ni and Zn.

CHAPTER 4 HEAVY METAL MOBILITY IN CONTAMINATED SOILS: PART 1. SOIL-OF- EXCHANGE SITES IN CONTROLLING MOBILITY AND MOBILITY OF HEAVY METALS

Introduction

Heavy metal mobility in soils is of environmental significance due to its toxicity to both humans and animals (Ma et al., 1990). As a natural water flow condition in a soil, heavy metal mobility is determined by its solubility. It has been well recognized that the solubility of heavy metals in soil is mainly regulated by adsorption, precipitation and ion exchange reactions. Although much effort has been spent to model heavy metal solubility (Christberg et al., 1983; Sparks, 1987), such a prediction under field conditions contains large uncertainty. It is partially because of the difficulty in measuring the effects of dynamic soil solution chemistry on heavy metal operations. However, changes in solution chemistry, such as pH, redox potential and ionic strength, may shift the retention parameters of heavy metals significantly. These impacts may be further complicated by the competition of various ligands, which may enhance heavy metal mobility under certain conditions (Amelunx, et al., 1994).

Soil redox status varies temporally and spatially. In a surface soil it is influenced by rainfall, humidity and changes in land use, whereas in subsurface soils mostly by fluctuation in water table (Jard et al., 1987). A reduction in redox potential may cause changes in metal-solubility rate, formation of new low solubility precipitates, and Fe

dissolution resulting in release of metals (Anderson et al., 1994; Chao et al., 1996; Maschke et al., 1991). To experimentally evaluate the effects of different water state on metal solubility, various techniques have been developed, under potential-controlled batch experiment using a suspension (Chao et al., 1996; Maschke et al., 1991), ultraviolet-irradiated (positive/ negative) irradiation (Amthor et al., 1994; Karszewski, 1996; Yu et al., 1995) and water-flooded dissolution (Karszewski, 1996). However, some contradictory results have been found when the different techniques were employed. In water-controlled suspension experiments, Chao et al. (1996) reported that aqueous concentrations of Pb, Cd and Zn increased with Fe(II) as water potential decreases, suggesting metal complex onto surfaces of Fe hydroxides or a dissolved phase is controlling aqueous metal concentrations. On the other hand, in experiments using saturated paste, Amthor et al. (1994) found that concentrations of Cu and Cd decreased whereas those of Fe(II) increased in solution as the water potential was decreased. However, in principle, it may be more Cu or Cd released can be proved under these conditions. Similar controversial results are found in other studies (Maschke et al., 1991; Yu et al., 1995). However, it should be pointed out that among the studies, the samples analyzed for metals were different. They can be classified into two groups. 1) past water and leachates from soil treated with DSW and 2) leachates separated from the suspensions and leachates from soil treated with electrolytes. Obviously, metals dissolved in leachates of the first group are more soluble relative those of the second group, outside the exchangeable in addition to water-soluble metals. Therefore, a natural question is raised: with leachates, do metal concentrations in solution change proportionally with those in exchangeable phase? To our knowledge,

the role of exchange phase in controlling the solubility and mobility of heavy metals in leached soils has not been reported. However, this knowledge may improve our understanding of the controversy discussed above.

In Chapter 3, Pb solubility was examined in a sandy soil spiked with Pb and leached for 48 h under water-flooded or non water-flooded conditions. Solution chemistry in soil columns was adjusted using different concentrations of NaCl and CaCl₂ and deionized water of varying pH before incubation. The results show that Pb solubility in the incubated soil can be related to the ratio of aqueous Pb to 0.1 M HCl extractable Pb (CE) from solid phase instead of soluble Pb alone. If we assume 0.1 M HCl extractable Pb(CE) shows the solid phase is proportional to exchangeable Pb (EX), it is suggested that exchange may have significant effect on heavy metal solubility in soils.

In this paper, we will extend our study from a synthetically contaminated soil to two naturally contaminated soils. In addition to Pb, concentrations of Cu and As will be presented for comparison. The major objective of this paper was to examine the role of exchange sites on the solubility and mobility of Pb, Cu, and As in soils during incubation.

Materials and Methods

Leaching and characterization of soil samples

The two Pb-contaminated soils used in this study were from Montreal, Canada and Tampa, Florida, which were exposed to Pb factory recycling and wastewater treatment operations in the past. Selected characteristics of the soils are listed in Table 4-1.

TABLE 4-1 Selected characteristics of the soils used in this study

Soil location	pH	C/NC	Organic C (%)	Particle size distribution (%)			Total element analysis (mg kg ⁻¹)				
				Clay	silt	Sand	Fe	Fe	Al	Si	C
Mexican	6.10	0.00	1.24	48	40	11	1400	17000	10000	800	11700
Canada											
Tampa, Florida	5.80	2.71	8.28	49	28	23	1100	1000	1500	20	1100

Column Experiments

Preparation of columns and leachate process. 50 g acid-washed sand (20-30 mesh) was packed in the bottom of 60-ml. columns (11-cm in length x 3.4-cm in diameter), then 30 g air-dried soil (percentages content = 9.8%) was packed on top of the sand layer. Preliminary data showed that the sand layer helps to prevent the surface clogging in a column during incubation and leaching as less an detectable impact on soil colloid mobility. During each step, the columns were gently shaken horizontally for a few minutes to minimize the packing effects. This resulted in 24 and 3 columns of 60-ml. columns for the blastomyl and Tempra soils, respectively. The soil columns were wet vertically and permeated by pumping deaerated distilled water (DDW) into the bottom of the columns until the water level in the columns was above the soil. These columns were then incubated under water-flooded conditions for approximately 3, 28 and 40 d for the Tempra soil and 3, 28, 36, 48, 36 and 40 d for the blastomyl soil.

Leaching. Once the water potential measured had reached to a certain level, the water on top of the soil column was removed and a rubber stopper was put on top to seal the syringe. The syringe was then turned upside down. The lower side of the column was connected to a needle as an inlet for the effluent, 0.01 M CaCl_2 . The pumping rate was $1.25 \text{ ml. min}^{-1}$. The effluent from the top of the column was collected with a fractionation collector.

Analysis of leaching. Each fraction of effluent was filtered through 0.22 μm membrane filter, then acidified to pH=2 to yield the soluble metal concentrations. The details can be found in Chapter 3.

Isolation of pore water of soil

To analyse metal concentrations in pore water an incubated first subsurface soil within the study incubation zone was used after removing the standing water on top. Pore water was separated from the soil by the centrifugation method described by Skarbo-Karna et al. (1982) and Das and Levy (1978). Then the pore water was filtered with 0.22-µm membrane filter for metal analysis. For detailed procedure of Fe(II) analysis, please see Chapter 3.

Results and Discussion

Changes in heavy metal solubility with incubation

Concentrations of heavy metals and Fe (II) in pore water varied with incubation time (Figures 4-1 and 4-2). Fe behaved differently in the two soils with incubation. In the Mondul soil, Fe(II) decreased with incubation (Figure 4-1) whereas in the Tumpu soil it increased (Figure 4-2). Similarly, Pb increased in the Mondul soil and decreased in the Tumpu soil with incubation. However, at both soils the concentrations of Zn (II) and Cu were inversely correlated with incubation (Figure 4-1 and 4-2). Concentrations of As and Cd increased first then decreased with incubation in the Tumpu soil.

In similar experiments by Ambrose et al. (1999) using soils incubated in water-flooding conditions, they found that Fe (II) concentration in pore water increases with incubation time. This is consistent with the results we found in the Tumpu soil, however it is contrary to that in the Mondul soil. With incubation, redox potential reduced and thus

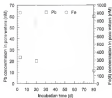


Figure 4-4. Released Fe (II) concentrations in pure water of the Montreal soil.

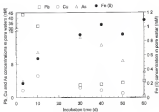


Figure 4-2: Concentrations of Pb, As, Cu and Fe(II) in pore water of Ba Tump soil

dissolved Fe(II) increased due to Fe(II) reduction to Fe(0) (Amthorn et al., 1994). However, the unexpected behavior of Fe(II) in the Measured well may be caused by formation of FeCO_3 , which will be discussed in Chapter 5 in detail.

Chen et al. (1994) examined the release of heavy metals from a contaminated soil, which was suspended in water (soil/water ratio = 1:10), and found that aqueous concentrations of Pb, Cd and Zn are positively correlated with those of Fe during incubation because heavy metals are released from Fe (oxy)hydroxide surface as it dissolves (Chen et al., 1994). Obviously, it is contrary to what we observed for Fe concentrations in both the Tampo and Measured wells. On the other hand, Amthorn et al. (1994) reported that, under water-saturated (soil/water ratio = 1:0.1) incubation, Cd and Cu concentrations in pore water decrease whereas Fe(II) increases with time. This is consistent with our results. It is possible that the different relations between Fe(II) and heavy metals in relation result from the different soil/water ratios used in different studies. In the studies discussed above, concentrations of exchangeable metals in aqueous metal concentrations during incubation varied with the soil/water ratio. When the ratio is low, i.e., small quantity of soil is suspended in large amount of water, then as the exchange rates tend to diffuse into the water to maintain their chemical potentials between solution and exchange sites. Consequently, the importance of exchange sites in holding metal ions releases is a relative sense. On the other hand, as the soil/water ratio increases, the importance of exchangeable metals in contributing to soluble metals increases because the amount of exchange sites increases relative to solution volume. Therefore, metal distribution between solution and exchange sites has to be taken into

concentrations, which is mostly controlled by metal competition between exchange sites and aqueous ligands in solution. Therefore, the observation of Jambon et al. (1990) and the one presented here may be due to the fact that, with exfoliation, more binding sites are available for exchange sites as Fe (II) concentrations increase in solution. We have demonstrated that Fe solubility in soil solutions is inversely related to aqueous Fe concentrations in Chapter 3. Therefore, in this sense, all the studies discussed above along with the one presented here are consistent, i.e., with Fe dissolution upon exfoliation, Fe is released into solution and exchange sites.

Similarly, arsenic concentrations in pore water and suspension varied differently with exfoliation. Mondalaya et al., (1991) examined the arsenic release from a contaminated soil as a suspension (pH water = 1.6) during exfoliation, and found that soluble arsenic increases as redox potential decreases (+500 -100 mV). It was attributed to $As(V)$ reduction to $As(III)$ and Fe reduction dissolution as release attributed to. However, analysis of pore water in soils after water flooded exfoliation showed a different trend (Coburn and Houser, 1986). They found that soluble arsenic concentrations increased first and then decreased with exfoliation, and a maximum occurred in 20-30 d after flooding. Further analyses of the solid phase showed the loss of soluble arsenic could be accounted by further leach when the soil was exfoliated longer than 20-30 d. The result of the later study is consistent with our data that showed As_2 concentrations increased and then decreased with Fe reduction-dissolution (Figure 4-2), which will be discussed in the following section.

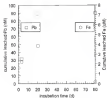


Figure 6.3: Cumulative Pb and Fe leached after 31.8 pore volumes of 0.01 M CaCl_2 in Montmorillonite.

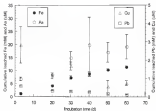


Figure 4-6 Cumulative Pb, Zn, Cu and Fe leached after 24 h pore solution of 0.01 CaCl₂ in Tempa soil

Heavy metal mobility with acidulants

Mineral acidity in this paper is examined using cationic resins loaded with 32 ppm values of 1.81 g/L CaCl_2 solution. It is well understood that the metals that can be loaded on with CaCl_2 solution include both the soluble and the exchangeable. For the Montreal soil, the cumulative loaded Fe concentrations increased with acidulation (Figure 4-1), which is consistent with the overall trend shown in the pore water (Figure 4-4). However, the cumulative loaded Fe concentrations showed a different trend than Fe(II) concentrations in pore water (Figure 4-2), suggesting that Fe(II) is exchangeable is not proportional to that in aqueous phase assuming that Fe(II) is soluble Fe. For the Tampa soil, changes in overall trends for metals with acidulation can be divided into two groups: 1.) Pb and Cu decreased with acidulation, 2.) Arsenic Fe increased with acidulation, which is not consistent with the case in pore water.

In fact, the reduction of cation-exchange capacity (CEC) caused by the adsorption of hydrous polymers at zero hydrous soils and mineral has been long recognized (Coleman and Thomas, 1964; Cernin et al., 1980). Henderson and Lachalade (1981) reported that Fe coatings alter the lower CEC and the cation exchange capacity (AEC) in comparison to the untreated case at pH 7. They suggested that the Fe coatings reduce the CEC and increase AEC measured at their pH by either physically blocking or electrostatically neutralizing the permanent negative charge carried by the crystalline minerals. Similarly, Arora et al., (1988) found that the point of zero-charge (PZC) of Fe-coated kaolinite increases linearly with the amount of the coating Fe. In the experiments by Skoldberg, et al. (1987), they demonstrated that the CEC of the untreated Fe (FeCl_3) and soil decreases by 22% as the 18 mmol Fe/L

treatment to 72% in the 40 mg/L Fe(II) treatment, and correspondingly the exchangeable sodium percentage from 12.8 to 12.4. Ruspensky and Oades (1977) reported that with addition of ferrous hydroxide the electrophoretic mobility of iron clay increases from negative to positive values. All these data support that with the reduction dissolution of Fe, Fe coating fraction decreases, and then CEC increases for a soil. Even though it is supported by sufficient experimental and theoretical evidence, it has, to our knowledge, not been stated for uncoated soils. However, the reduction in CEC, along with relative chemistry, may have significant effects on heavy metal retention.

With the reduction dissolution of Fe, therefore, the blocked-exchangeable sites will be freed and the concentration of Fe in pore water increases, and then Fe (II) concentration in exchangeable phase may increase as well. It was evident that, for the Tump soil, changes in Fe (II) concentrations in pore water and its cumulative leached amount with incubation time were similar (they both increased) with incubation (Figure 4-4). However, for the Irbid soil, a smaller increase in cumulative leached Fe was found at 30-day incubation compared to Fe (II) concentrations in pore water, suggesting that exchangeable Fe (II) became dominant in cumulative leached Fe. In fact, there was 1.10 pmol/L Fe leached during 7.14 pore volumes (which can be considered as exchangeable) among 7.18 pmol/L of the total cumulative leached Fe after 30-d incubation.

In the Tump soil, changes in Pb concentrations in pore water and its cumulative leached Pb with incubation time were similar (they both decreased) with incubation. This is contrary to Fe behavior, suggesting that Pb concentrations in solution may be controlled by competition between aqueous Fe and Pb for ligands and exchange sites. In

is well documented that Fe(II) and Pb(II) have similar affinity for ligands (Turner et al., 1981; Nielsen and Richard, 1986). As aqueous Fe(II) concentrations increase with incubation due to Fe reduction dissolution, more aqueous Pb(II) may be forced into exchange sites. If this is simply the case, however, the cumulative leached-Pb was not supposed to decrease with incubation (Figure 4-4). However, it was difficult to imagine that there was so much Pb present in the exchange sites without some of it adsorbing externally onto the surfaces. However, it should be pointed out that there was significant difference between the relations of Pb concentrations in pore water and cumulative leached-Pb with incubation: while for Pb concentration in pore water decreased exponentially the cumulative leached-Pb decreased only linearly (incubation time < 30 days). It is suggested that less reduction of the cumulative leached-Pb than that of Pb concentration in pore water could be caused by more exchangeable Pb with incubation.

In the Tux pe soil, cumulative leached Cu decreased with incubation (Figure 4-4), which is inconsistent with changes in Cu concentrations in pore water (Figure 4-2). The significantly greater cumulative leached Cu after 3-d incubation can be attributed to more Cu moving from exchange sites when leached with CuCl_2 . In fact, Cu(II) has greater affinity for exchange sites than Pb(II) (McCarthy, 1984).

Interestingly, As concentrations in pore water increased first and then decreased with incubation, whereas the amount of cumulative leached As showed no significant drop with incubation (Figure 4-4). As discussed above, as Fe "corrosion" was reversed with incubation via reductive dissolution, soil CEC increased as well. This caused more Pb(II) to transfer from solution to exchange sites, as a result, local change reversal might

occur, therefore positively-charged particles hold more $H_2AsO_4^-$ and/or $H_2AsO_3^-$. It has been realized that at slightly reducing conditions and $pH \approx 4$ (for the Thompson and Ineson study) both $H_2AsO_4^-$ and $H_2AsO_3^-$ are not stable thermodynamically (Culver and Franken, 1989). However, local pH near positively-charged surface may be significantly greater than in bulk solution: therefore $H_2AsO_4^-$ may be stable near highly positively-charged surfaces. On the other hand, there has been evidence showing that even under reducing conditions only $H_2AsO_4^-$ is associated with natural particle surfaces (Jolliffe and Turner, 1989). The existence of $H_2AsO_3^-$ under reducing conditions has been attributed to the oxidation of arsenite to arsenate by Mn and Fe oxyhydroxides (Patterson and Cooper, 1981).

As discussed above, CEC increases with Fe reduction dissolution, especially at $pH < PZC$ of Fe minerals. The consequent optimization of contacts between solution and exchange sites is probably determined not only by the magnitude of CEC, but also the distribution of metal ions, the competing anions and cations (especially). Therefore, changes in metal concentrations in a soil solution with time under incubation can be complicated. However, the following interactions have to be taken into consideration.

1. Fe reduction dissolution releases Fe(II) and solubilized heavy metals into solution at the same time lower exchange rates,
2. Fe (II) and heavy metal cations compete for ligands in clay or solution,
3. Fe(II) and heavy metal cations compete for the exchange sites, transferring from solution to solid phase.

4. Charge reversal on exchange sites results in negatively charged heavy metal²⁺ transfer from solution to exchange sites

In a particular soil system, different processes may be dominant in controlling metal concentrations in soil solution.

There is an alternative explanation for the As behavior with incubation. It has been well established that PO_4^{3-} may precipitate with Fe^{2+} to form minerals such as vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) in low soil redox potential (Hollibaert and Patrick, 1979; Patrick and Khalil, 1979). Because of the great similarity between H_2PO_4^- and H_2AsO_4^- or $\text{H}_2\text{AsO}_4^{2-}$, it can be inferred that formation of a new solid phase by Fe^{2+} and H_2AsO_4^- or $\text{H}_2\text{AsO}_4^{2-}$ limited the solubility of As as pore water in the incubation time approached to 50 days (Figure 4-4).

Implication of this research

In literature, there has been a big amount of papers focusing on changes in solubility and mobility of heavy metals with incubation. However, reported data have often been contradictory partially because of differences in soil/water ratios used in different experiments such as metal concentrations determined in pure water, filtrates reported from soil suspensions, and incubates (bottle and leached with DSW or an electrolyte). It has been noticed that concentrations changes of heavy metals with incubation are often confusing. For example, metal concentration in pure water or metal solubility limited by DSW suddenly decreases with incubation when occurrence of precipitation can not be proved. As discussed in this chapter, the roles of exchange sites in controlling metal concentrations in these systems have to be taken into consideration. With sufficient evidence, we showed the CEC of a soil change with incubation, and then

may greatly affect metal solubility and mobility. The role of exchange sites on the solubility and mobility of heavy metals is crucial to understand various behaviors of heavy metal upon sorption. Furthermore, incorporation of these results into future metal transport models may improve their accuracy.

CHAPTER 1 HEAVY METAL MOBILITY IN CONTAMINATED SOIL: PART 2. COLLID- FACILITATED METAL MOBILITY IN A Pb-CONTAMINATED SOIL

Introduction

Understanding metal mobility in soils is of significant environmental interest. In general, it is widely accepted that metal mobility, such as Pb, is practically negligible in soils due to their low solubility. However, enhanced Pb-mobility occurs in soils under certain conditions (Pernot et al., 1992). Colloid-facilitated metal-transport in soils has been proposed as one of the mechanisms (McCarty and Franken, 1989).

Colloids, e.g. clay, organic matter, and quartz, are ubiquitous in soils. Several processes responsible for colloid release and deposition have been well established. Based on the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory (Derjaguin, 1942), the net surface interaction energy is equal to the sum of the interactions between electrical double layer (EDL) and van der Waals forces, which control such separation distances. As particles move close to each other, the net interaction energy experiences a secondary maximum first, then a primary maximum after an energy barrier. After that point, further particle move towards each other causes drastic increases in the interaction energy, which is referred to as from repulsion. In principle, particles are attached (deposited) due to the net attractive forces as either the primary or secondary energy minimum. On the other hand, both the magnitude of the energy barrier and the separation between the two primary and secondary minima are affected by solution chemistry. In order for a deposited particles to release, repulsive forces have to be

potential) between surfaces of solid and stationary solid phases such as resulting from changes in solution chemistry. Changes in solution chemistry may induce or effluence the primary or secondary maximum so that the advent of deposited particles becomes frequent (McDermott-Bayer, 1993; Ryan and Gindoff, 1994). Numerous studies have shown that solution chemistry is one of the primary factors affecting particle deposition and release in natural porous media (Klenzendorf and O'Melia, 1990a; Lindstedt, 1993; McDermott-Bayer, 1993; Ryan and Gindoff, 1994; Serrano et al., 1995). However, influence of solution chemistry on the interaction between EDLs of particles is a rather complicated issue. In addition, solution chemistry is not uniform spatially and temporally. Therefore, it is still a challenge to model the interaction of EDLs between colloids and stationary solid phases in soils.

Nevertheless, effects of solution chemistry on colloid mobility are closely related to potential-determining ions (PDI, PDI), specific adsorbed ions (PDI, SIT) and indifferent ions (PDI, IIT) present in soil solution. Potential-determining ions are constant ions of solid particles (e.g. H^+ and OH^- of Fe oxides, Ca^{2+} and CO_3^{2-} of $CaCO_3$) and their concentrations primarily determine particle surface potentials. Specific adsorbed ions are those adsorbed onto solid surfaces and may change the magnitude and even sign of the surface charge (e.g. Ca^{2+} and Pb^{2+}), whereas indifferent ions are those adsorbed physically to surfaces and change only the magnitude of the surface charge (e.g. Na^+ and Cl^-). It is important to consider all three types of ions when studying the impacts of dynamic solution chemistry on colloid mobility in soils. In surface soils, solution pH, ionic strength and water potential are influenced by rainfall, humidity, or change of land use, whereas in subsurface they are mostly influenced by the fluctuation of water

ratio (Bard et al., 1977). In other words, as one of these kinds of ions (potential determining ions, specifically selected one and sufficient ions) vary drastically with time and space in terms of species and concentrations, inevitably, these changes will significantly affect the interactions between colloidal surfaces and stationary solid phases, and thus colloid release and deposition.

In particular, solution chemistry has great effect on surface charge heterogeneity of soil. Grades of Fe, Al and Mn are the most common sources of surface charge heterogeneity in natural aqueous environments (Ryan and Blumhagen, 1996). At neutral pH, these compounds may carry a positive surface charge, which are called positively-charged patches in various minerals such as quartz and feldspar that carry negative surface charge (Singer et al., 1994). In natural aqueous systems, the range and magnitude of the valences of these patches may affect colloid deposition and release significantly. Recently, Johnson et al. (1998) have demonstrated that colloid deposition rate is controlled by the extent of positively-charged patches developed on stationary solid phases in porous media. In dynamic soil environments, however, these patches may vary temporally and spatially with solution chemistry (e.g. pH and redox potential) greatly affects colloid mobility. However, the effects of the dynamic feature of surface charge heterogeneity on soil colloid mobility are not considered in most studies.

Mobile of ions relatively tend to associate with colloids (Mills et al., 1991). They may adsorb or precipitate onto colloidal surfaces, or even form their own colloids. Take Fe^{2+} for example, in the first case, Fe^{2+} may affect the surface potential between solution and solid electrically by acting as a specific selected ion (Kornfuss et al., 1993). In the second case, Fe^{2+} is a potential determining ion that may change the surface potential

greatly. In other words, the mobility of these colloids may be different from the expected ones during charge development. The mobility of metal-bearing colloids thus needs to be examined (Toussaintjeff et al., 1997; Kerekes et al., 1997).

The objective of this study was to evaluate the effects of soil solution chemistry on colloid-facilitated metal mobility, such as Fe, Al, and Pb, in a Pb-contaminated. Such effects were limited to those arising from surface properties of colloids and stationary solid phases, which are impacted by soil solution chemistry. In our experiment, soil solution chemistry was altered through incubation under various conditions. After preincubating the soil columns with 4–10 μM CaCl_2 solution, the effluent was switched to deionized water (DDW) to mobilize colloids. Such columns were shown to avoid colloid redeposition. Our results showed that colloid mobility varied significantly with incubation, which may be caused by changes in surface charge heterogeneity on colloids and stationary solid phases.

Materials and Methods

Characterization of soil samples

The lead-contaminated soil used in this study was collected from Montreal, Canada. The site was contaminated via Pb battery recycling and subsequent washing operations in the past. The soil was air-dried and passed through 2 mm sieve. Total elemental composition of the soil was determined with a Thermo-Jacob-Ash 610 ICP after digestion in a CEM MDS-2000 microwave using EPA standard 3051. The soil was also analyzed using x-ray diffraction and thermal analytical techniques, as

Table 3-1 Selected properties of the Fe contaminated soil used in this study

Soil location	Mississauga, Canada
pH (1:1 with distilled water)	7.9
Fraction of organic carbon	2.54
Total Elemental Analysis (Ino, 1990)	$\mu\text{g kg}^{-1}$
H	1.48
Fe	150.38
Al	189.58
Mn	0.88
Cu	15.78
Particle size distribution (Day, 1965)	%
sand	33
silt	40
clay	40

thermogravimetry and differential thermal analysis. The major minerals present in this soil include Fe-oxides(hydroxides), quartz, calcite, dolomite, vermiculite, mica, and illite/musc. Selected soil properties are shown in Table 3.1.

Column Experiments

The experimental 1:1 combination of Chapter 4

Location: After displacing the original soil column as described in Chapter 4, the column was refilled to [KPF]. The effluent from the top of the column was collected with a fractionation collector. Turbidity and pH in the effluent were determined immediately.

Analysis of effluent: Each fraction of effluent was split into two parts. One was acidified with HNO₃ to pH < 2 without dilution. The metal concentrations determined this way are termed as total metal concentrations, (sum of colloidal and soluble Fe). The second part was acidified to pH=2 after filtering through 0.1 μ m membrane filter to obtain dissolved metal concentrations.

Analysis of Fe(II) and Ca in pore water

Redox potential naturally decreases with distance under water-saturated conditions. In one study, the electrode installed in soil columns measured redox potential only in a relative sense as discussed previously. In addition, Hansen (1984) suggested that it is more reasonable to measure important redox species than redox potential to indicate redox status in natural systems. Fe(II) concentrations in pore water was thus used as a measure of redox status.

Port water was separated from the soil by centrifugation (Shiota-Kishi et al., 1982; Cao and Lary, 1978) after removing standing water on top of the soil columns. The pore water was then filtered with 0.1-µm membrane filter for metal analysis. Aliquot of 0.1 mL of the filtrate was transferred (0.01 mL of benzene C₁₂L₁₀ or 0.01 mL HEPES (2-(4-(2-hydroxyethyl)pyridine)-N-(3-sulfonethyl)acid) buffer at pH=7 (Lovely and Pridge, 1983; Haron et al., 1994). Concentration of Fe (II) was determined by measuring the absorbance of the filtrate at 542 nm (Stookey, 1976). In addition, Cu concentration was determined by atomic absorption spectrophotometer.

Analytical methods

All experiments were conducted in duplicate or triplicate (95% H₂O₂)
labware: All glassware used in this study were of analytical grade or better. Double distilled water from a Barnstead NANOpure water system was used. Total metal concentrations of the filtrate were analyzed with an atomic absorption spectrophotometer (Folio-Glove L180) equipped with a graphite furnace atomizer. Flame atomic absorption was used to analyze metal concentrations > 1 mg L⁻¹ and graphite furnace atomizer was used to measure metal concentrations < 1 mg L⁻¹. Multi-level standards (Folio Scientific) for all metals were prepared in the same matrix as the extracting reagents to minimize matrix effects. Blanks were used for background correction and other sources of error. At least one duplicate and one spike sample were run with every 20 samples to verify method precision. The spike recovery and precision were found to be within 100% ± 10%.

Result and Discussion

Colloid release and adsorption

Effluent turbidity, a measure of relative colloid concentrations, generally decreased with incubation time, with longer incubations resulting in lower turbidity (Figure 3-4). Maximum turbidity was reached at 3-4 pore volumes for all soil columns, suggesting that colloids were mobilized by switching the effluent from 0.01 M CaCl_2 solution to DCM. Effluent turbidity stayed more or less constant as pore volume increased from 3-4 to 24. Chloride concentration, which was 20 mM in the influent influent results in DCM, decreased significantly from 20 to 0.2 mM as pore volume increased from 5 to 1-8. Meanwhile, the turbidity increased drastically from 0.2 to 0.8 NTU. It is suggested that colloids were mobilized by DCM immediately while 0.01 M CaCl_2 in the soil columns was displacing by DCM. This fast colloid release has been reported by Huan-Guo et al. (1994) who observed that polystyrene latex was released from a silica sand column due to reduction of ionic strength in the effluent. They explained that reduction in ionic strength may eliminate prior-set attractive forces (primary or secondary) so that colloid release rate is fast relative to the advective solution flow through the column.

As indicated by turbidity, colloid mobility decreased with incubation or with decrease in aqueous $\text{Fe}(\text{OH})_3$ concentrations from 0.01 to 0.17 $\mu\text{g/L}$ in pore water (Figure 3-5A). The cumulative leached colloidal Fe at 24 pore volumes after 3-4 incubation (aqueous $\text{Fe}(\text{OH})_3 = 0.01 \mu\text{g/L}$) were significantly greater than they were after 28- or 80-d incubation ($\text{Fe}(\text{OH})_3 = 0.27$ or $0.17 \mu\text{g/L}$) (Figure 3-5A). It has long been recognized that

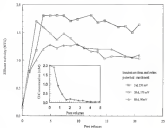


Figure 5-1 Changes of effluent salinity with port inflow under different retention times. The inset is a typical breakthrough curve of Cl^- when dechlorinated water displaced CaCl_2 .

redox status may affect colloidal mobility in soils (McCarthy and Ziemann, 1988; Gaddeland et al., 1994). However, there is little information available on this topic in the literature. In Fe-oxide-coated sand, Ryan and Gschwend (1994a) released particles with washed soil to observe an elution effect, and found that the amount of colloids in effluents is directly related to the concentrations of dissolved Fe. This is seemingly consistent with our result as the colloidal colloidal Al and Fe were proportional to aqueous Fe (II) concentrations in pore water (Figure 3-2A, $r^2 = 0.93-0.97$).

In this study, redox status decreased with incubation, which was confirmed by decrease in redox potentials measured (Figure 3-2). In general, a more reducing condition produces a greater aqueous Fe concentration (Chen et al., 1994). In our system, however, the opposite was observed, i.e. aqueous Fe (II) concentrations in pore water decreased from 8.91 to 0.17 μM as incubation increased from 3 to 30 d, suggesting that decreasing by redox status of Fe-oxide may not be the only factor controlling redox mobility in our system.

Though the Fe (II) concentration in pore water decreased with incubation, it did not change much when the incubation time was increased from 20 to 30 d (Figure 3-2), suggesting that Fe concentrations may be controlled by mineral solubility in the period. From a thermodynamic point of view, solubility of FeCO_3 can control Fe^{2+} solubility in soil depending on redox conditions and CO_2 concentrations (Lindsay, 1979). In this study, soil redox status became more reducing with incubation, which was confirmed by redox electrode measurements (Figure 3-2). Therefore, aqueous Fe (II) was released by Fe reduction dissolution. The soil used in this study contained ~8% of calcite (CaCO_3 , log $K = -9.74$), which is much more soluble than siderite (log $K = -7.61$, Lindsay, 1979). In

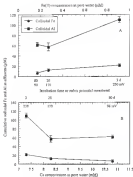


Figure S-2: Balance of species Fe (a) and Cu concentrations in the pore water of red column on the permeable colloidal Fe and Al concentrations in the effluent after 22 pore volumes during sorption.

this case, formation of siderite was favored as a stable iron mineral, which was confirmed by MINTEQA2 calculation (Allison et al., 1991). This may explain why aqueous Fe(II) decreased as incubation time increased.

When iron oxide present in the soil used in this study carried mostly negative charges as expected (Table 3-2). The minerals carrying pH-dependent charge, their point of zero charge (PZC) was generally lower than $\text{pH} = 7.7$ of the soil (Table 3-2). The variable surface is the zwitterion has (-) potential ~ -0.1 meq at 0.1 M NaCl . These evidence supported that the soil was negatively charged, however, the positively-charged patches may also exist. It is commonly believed that Fe oxides are major sources of positive charge near neutral pH. This led us to expect that as more Fe oxides dissolved with carbonate, positively-charged patches decreased, and soil mobility would increase. However, the opposite relation between incubation and Fe(II) concentrations were observed in this study (Figure 3-24).

As discussed previously, Fe oxides may be transformed to siderite. This transformation provided superior Ca concentration at pilot water, which was consistent with the fact that Ca concentrations increased with incubation (Figure 3-25). On the surface of carbonate minerals, there are different examples (Charet et al., 1990; Cappelletti et al., 1991) showing that the positive-charge development can be mainly described as



where $\text{>CO}_2\text{H}^0$ and $\text{>CO}_2\text{M}^+$ stand for carboxylic sites and its complexes with divalent cations (M^{2+}) at the surface of carbonate, respectively. In our system, Ca^{2+} was dominant among all the M^{2+} in pilot water. For example, Ca concentrations was much greater

Table 5-3. Minerals at the well and their Point of zero charge (PZC)

Minerals	PZC	Reference
Yerkesite		
Illite		
Feitingsite		
Fe oxides (amorphous)	7.5-8.1	Dronkers <i>et al.</i> , 1990
Quartz	5-3	Petuk 1967
Calcite	5.5-6	Petuk 1967
Dolomite	8.8	Petuk 1967

than $\text{Fe}(\text{OH})_3$ (Figure 3-2). In addition, no changes in pH along and column were found ($\text{pH} \approx 7.7$), which may be due to the buffering capacity of calcite. Nevertheless, the given as a basis to assume Ca^{2+} concentrations were proportional to that of apatite Ca in the pore water. Obviously, Eq. (3-7) suggested that the positive-charged patches on calcite increased with aqueous Ca concentrations and that that colloid stability decreased because more calcite colloids had deposited on the calcareous grains with a greater binding (Germany maximum deposition). This is consistent with the observation that colloidal Al and Fe were inversely related to aqueous Ca (Figure 3-2, $R^2=0.43$ and 0.38 , respectively).

Colloid attachment

Concentrations of colloidal Fe and Al changed with pore volumes are demonstrated in Figure 3-3. Different from the observations made in well-defined systems (Nicolis-Gabel et al., 1994) that the classic curves consists of one major narrow peak, the colloidal metal concentrations peaked over a wide range of pore volumes or repeatedly at several numbers of pore volume. It has confirmed that the patterns of the elution curves are reproducible. The velocity difference between fluid (pore) and colloidal particles have been long recognized (Smed, 1974). Size exclusion of colloidal particles could occur faster or more faster than the water. On the other hand, colloid deposition on a secondary calcite can may retard colloids significantly (Nicolis-Gabel et al., 1994). To our knowledge, however, no phenomenon has been reported that colloid eluted in the manner as shown in Figure 3-3.

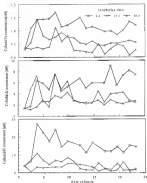


Figure 5-1 Eluent curves of effluent Pb, Al, and Fe concentrations in effluent with pore water under various incubation times. Each point represents the mean of two replicates.

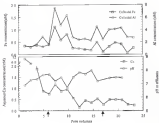


Figure 3a Relationship among colloidal Fe and Al concentrations, dissolved Ca concentrations and pH in effluents after 5 d of incubation. Each point represents the mean of two replicates. The trend is reproducible. The arrows indicate the boundary beyond which the Ca release mechanism from the soil may change.

In fact, after the displacement of the original wall solution in a well column with 0.01 M CaCl_2 solution, Ca was the dominant cation in both bulk solution and electrical double layers (EDLs) surrounding colloidal particles and stationary solid phases in the well. When the effluent was switched from 0.01 M CaCl_2 solution to DOW, we expect that the release of Ca from the well be dominated by viscous mechanisms, which come to play probably in a later sequence. At the beginning stage of switching to DOW, the release of Ca from the bulk solution, which was controlled by the fact that Ca concentrations and pH in the effluent in pore solution = 1 were approximately equal to those of the effluent ($[\text{Ca}^{2+}] = 0.01$ M, $\text{pH} = 6.95$) (Figure 3-4). Secondly, Ca diffusion from EDLs in the bulk solution driven by a concentration gradient may become dominant as the number of pore volumes increased between the two curves in Figure 3-4). When Ca in the bulk solution was depleted, Ca cations moved against electrostatic attraction away from the surfaces driven by osmotic pressure, extending EDLs surrounding colloids and solid phases to release calcium. Obviously, any significant expansion of EDLs and resultant colloidal destabilization had to be associated with significant amounts of Ca released into bulk solution. In this case, the excess Ca^{2+} in the depleted bulk solution may be associated with hydroxyl to release proton ($\text{Ca}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CaOH}^+ + \text{H}^+$) (Olsen and Munksgaard, 1977), resulting in a decrease in pH. Between pore volumes 4-11, significant increase in Ca concentrations and decrease in pH accompanied significant increase in diffused concentrations (Figure 3-4). This is consistent with the two features we proposed above. Generally Ca hydrolysis is weak at relatively low pH, so it is not likely that a low pH drives as much as 1 unit in shown in Figure 3-4. In a heterogeneous system such as an

this study, however, the deficiency of negative charge related to the bulk solution, hence it was possible that the charge deficiency may further drive dissolution of H_2O , releasing protons. Thirdly, desorption of Ca from soil surfaces and stationary solid phases occurred from 18 to 23 pore volumes (after the second burst in Figure 3-4). This was a slow process and therefore occurred at high pore volumes, resulting in no significant irregularities between effluents and stationary solid phases. An increase in Ca concentrations and in pH were observed in the effluent at pore volumes between 17-23 (Figure 3-4). In essence, this process is equivalent to sorbed Ca displaced by H^+ . However, a direct evidence is needed.

Obviously, dissolution of Ca minerals in the soil may also play a role in regulating the release of Ca from soil columns, especially during pore volumes of 18 to 23. During pore volumes of 1 to 23, however, it was impossible for dissolution to play a significant role in Ca releasing, because the pulse-like feature of Ca releasing cannot be explained by dissolution of Ca minerals. Of course, overlapping between the different stages may occur. However, each individual mechanism may dominate a particular range of leaching (Figure 3-4).

As discussed above, the effluent elution curves can be roughly divided into two regions between pore volumes of 1-23, which were regulated by Ca diffusion or desorption (Figure 3-2). This suggested that a wide range of surface heterogeneity existed at soil colloids and stationary solid phases. In theory, different from the colloids controlled by Ca release via desorption, those controlled by diffusion must contain less amount of reactive groups such as $-\text{CO}_2\text{H}$, OH on the surfaces. However, there was no direct evidence to support this conclusion in this study. In the range of Ca diffusion,

colloid release showed a clear diurnal pattern. In a well-controlled system, Nordin-Gabell *et al.* (1996) have demonstrated that polyisoprene colloids are released from the volume packed with silica sand in a similar manner, i.e. no pore volumes increased colloid concentrations appeared as two-peak-like peaks. They attributed these to the inherent heterogeneity of the silica sand matrix and suggested the two separate peaks are most likely related to the primary and secondary deposition of colloids. In our study, the interactions between colloids and secondary solid phases are much more complicated because of the heterogeneity of both colloids and secondary solid phases. Therefore, one may expect that soil-colloid release would manifest themselves in a chromatographic manner since each group of colloids, which possess similar surface properties, would appear as two peaks or effluents, which is caused by colloids releasing from the primary and secondary depositions. This is consistent with the trend of pore volumes less than 17 shown in Figure 3-3.

As shown in Figure 3-3, colloid mobility changed with condensation rates. However, the peak positions of colloid concentrations under different incubation basically matched each other, even though some shifted slightly (Figure 3-3). This suggested that condensation did not significantly change the major types of mobile colloids and their mobility when it affected the relative population of each type colloid when they were exposed to a common permeation.

Colloidal Fe and Al mobility

Similar to colloidal Fe and Al, colloidal Pb concentrations varied with incubation (Figure 3-3). Interestingly, there was no significant difference in the colloidal Fe and Al in the first several pore volumes when the columns were incubated from 1 to 20 d (Figure

3–5), while the concentrations of colloidal Pb decreased appreciably 4 times after 20-d flow-bed incubation (Figure 3-1). This suggested that Pb-binding-colloids tended to be immobilized in the presence of anoxia, and of Pb with mobile colloids decreased with water-flooded incubation. However, a recent research (Kucuktemur et al., 1997) suggests that the association of Pb with colloids does not affect colloid-mobility significantly, especially at low surface coverage. This may exclude the first possibility.

It is well known that Pb is most likely sorbed onto Fe oxides (Benjamin and Loefer, 1981). However, when the environment becomes reducing, Pb is released as Pb oxides dissolve (Custrell et al., 1988). This suggests that Pb sorbed by mobile colloids may redistribute with incubation. One possibility is that the released Pb sorbed onto the surface area (carbonate (CO_3^{2-}) of carbonate minerals (Zachara et al., 1994), and the particles bearing carbonate mineral may carry positive charge and are tend to be immobilized as discussed before. Therefore, colloidal Pb decreased with incubation. However, further study is needed to verify this mechanism.

Conclusion

In this Pb-contaminated soil, colloid mobility decreased with incubation, and it was positively and inversely correlated to the concentrations of dissolved Fe and Ca in the pore water, respectively. This cannot be understood by either the decreasing effect from reducing dissolution of Fe oxides and charge heterogeneity among them. Instead, it is possible that the decrease of colloid mobility with incubation was caused by an increase of positive-charged patches of carbonate surfaces, which is determined by Ca^{2+} concentration in pore water.

A distinct pattern of cellolysed Fe and Al concentrations changes with post release was observed. In general, a peak of cellolysed release accompanied a higher dissolved Ca concentration. Three possible mechanisms, i.e., bulk solution displacement, diffusion out of ECR, and desorption from surfaces, were proposed and played a major role at a time sequence in Ca release. These mechanisms may explain the characteristic pattern of cellolysed Al and Fe concentrations changes with incubation time. Colloidal particles can facilitate Fe transport, however, the ability decreased with water-flooded conditions for this soil. It is possible that Fe redistribution from Fe-solids to solution occurred during incubation.

CHAPTER 6 RELEASE AND DEPOSITABILITY OF COLLOIDS IN TWO-CONTAMINATED SOILS

Introduction

Colloids, which are defined as particles $<1\mu\text{m}$, are ubiquitous in soils. Under certain conditions they may be mobilized and facilitate transport of heavy metals in soils (McCarthy and Zastrow, 2000; Newman et al., 1990), possibly imposing a threat on the environment.

Net release of colloids from a soil is mainly determined by rates of two opposite processes: colloidal release (Kralley et al., 1982) and deposition (Adamczyk et al., 1993). These processes are mainly controlled by the net surface interaction energy between colloids and stationary solid phases, which can be described by the DLVO theory (Derjaguin-Landau-Verwey-Overbeek) (Israelachvili, 1982). Based on the DLVO theory, the net surface interaction energy is equal to the sum of the interactions between electrical double layer (EDL) and van der Waals forces, which vary with the separation distance between colloids and stationary solid phases (Figure 3-1). As colloids move close to stationary solid phases, the net surface interaction energy experiences a secondary maximum first, and then a primary maximum (β_{max}) after a minimum energy barrier (β_{min}). After that point (β_{min}), further movement of colloids towards the stationary solid phase causes drastic increases in the interaction energy, which is referred to as the Donnan repulsion. Consequently, particles are deposited when the net attractive forces are at either the primary or secondary energy maximum. Colloidal deposition is considered as a

two-step process: transport of colloids from bulk solution to the stationary solid surface and their attachment to the surface, which depends upon the nature of particle-surface interaction. Colloid attachment rate is exponentially related to the maximum energy barrier ϕ_{max} (Chakraborty and Pelevin, 1990). Similar to colloid deposition, colloid release also consists of two consecutive steps: detachment from the surface and transport to bulk solution, and the detachment rate is exponentially related to the depth of the energy well ($\phi_{max}-\phi_{min}$) (Figure 2.1).

To validate the DLVO theory in describing colloid deposition and resuspension in a suspension, colloid stability testing using batch experiments was developed (Kordecki and Overbeck, 1984a and b). Such a test has been partially adopted to evaluate the intermediate testing of colloids, i.e., water dispersibility of soil colloids (Jalili et al., 1995; Skoczberg et al., 1997). In general, water dispersibility of soil colloids decreases with ionic strength at a given pH. There is a critical flocculation concentration (CFC) of electrolyte for a given soil suspension, above which flocculation occurs. There has been effort to relate this CFC-based dispersibility of soil colloids to their mobility in soil (Kaplan et al., 1994; Seta and Kumbakonur, 1993; Skoczberg et al., 1991a and b) by applying batch-experiment based results to predict colloid behavior in column experiments since colloid stability tests are normally conducted in batch experiments whereas colloid mobility tests are done in column experiments. Tests with higher CFC may have greater colloid mobility since colloids can be more stable in a suspended state at a given condition. However, no consistent result was achieved when the CFC of soil dispersions they was used to predict soil colloid mobility (Kaplan et al., 1994). They recommended that CFC predicts colloid dispersibility, but not mobility when not assuming

is dominant in controlling colloid deposition, which occurs when colloid particles are larger than pore opening in porous media. Different from the colloid stability test, in which colloid deposition/aggregation is dominant, colloid mobility is a test in which colloid release rate of colloids in a given flow medium is shown in Eq. (5-1).

$$\text{Immobilized colloids} \xrightleftharpoons[\text{Deposition}]{\text{Release}} \text{Mobile colloids} \xrightarrow{\text{Transport}} \text{Colloids released } (R-C)$$

Colloid release can be induced by a rapid reduction of colloid chain strength in well-defined porous media (Rochester and Pories, 1976; Ray and Debnis, 1986a; Nordin-Giblin and Tobiason, 1988) and soil (Graham et al., 1982; Jacobson et al., 1987). However, this may not always be the case since the opposite result was also observed by Kallay et al. (1987). They attributed to the observation of colloid redeposition on short retention to a possible cause for flow observation. This suggests that the net colloid released often is a result of both colloid deposition and release. The effect of ionic strength reduction on colloid release has been attributed to the repulsion between colloids and porous media arising from EDL expansion, resulting in a reduction in the depth of the energy well (Kallay et al., 1987). Different from colloid deposition, however, colloid release is more difficult to evaluate both theoretically and experimentally. Using isotropic columns and quartz columns, Ryan and Olfendick (1984) have shown that the transport of detached colloids in the bulk solution is the rate-limiting step during rapid colloid release when the maximum energy barrier (Q_{max}) approaches zero (Figure 2-1). In fact, a similar phenomenon has been observed by Jacobson et al. (1987) in an intact column experiment in which the colloids were leached with tap water. By considering that

with the assumption that the net colloid release rate is determined by the relative rates of colloid release and deposition as shown in Eq. (4-1), one may conclude that, at a rapid release condition, the net colloid release rate is determined by the rate of the net colloid diffusion to bulk solution and attachment onto stationary solid surfaces.

Based on the above discussion, we hypothesize that, under a given water flow condition in a soil, the net colloid release rate may be controlled primarily by colloid attachment rate, which can be evaluated using the colloid stability ratio (W) as a comparison. Colloid stability ratio is the ratio of colloid flocculation rate of a suspension in natural-observation-conditions (pure suspension) to the faster rapid flocculation condition when the energy barrier (ΔE_{max}) = 0 (Kornik and Dzidek, 1954). Under slow flocculation conditions, only a fraction (W) of colloid collisions leads to coagulation. In fact, CPC represents only a special case of flocculation kinetics where $W = 1$. Therefore, W instead of CPC will be used to evaluate flocculability of soil colloids in this paper. Assume that the rate of flocculation is related to the changes in light absorbency of colloids, W can be obtained by dividing the rate of absorbency change observed at rapid coagulation condition by that at slow coagulation conditions (Kornik and Dzidek, 1954). In soil, measurement of light absorbency has been widely used to evaluate CPC of colloids (Hed and Sparks, 1982; Kottmann et al., 1987).

We have demonstrated that colloid release from soil columns is influenced by soil water status (Chapter 3), which cannot be simply related to the desorbing effect of Po ratios. Instead, colloid release can be related to changes in water potential determining flow and changes in soil index potential. In this paper, a different approach will be taken. We will (1) evaluate colloid dispersibility by comparing release colloid stability ratios;

and 2) determine the relation between the relative cation stability index and cation release in two selected contaminated soils.

Materials and Methods

Column preparation

The two Pb-contaminated soils used in this study were from Montreal, Canada and Tampa, Florida, which were exposed to Pb battery recycling and associated smelting operations in the past. Selected characteristics of the soils are listed in Table 4-1.

Soil columns were prepared as previously described (Chapter 4) and were initially columned here. 50 g of soil washed sand (70-90 mesh) was placed in the bottom of 60-ml. columns (13 cm in length x 2.4 cm in diameter), then 10 g air-dried soil was placed on top of the sand layer. This resulted in 2.4 x 2.2 and x 7.5 cm soil columns for the Montreal and Tampa soils, respectively. The soil columns were not vertically and permeated by pumping deionized distilled water (DDW) into the bottom of the columns until the water level in the columns was above the soil. These columns were then incubated under water flooded conditions for approximately 1, 10 and 60 d for the Tampa soil and 1, 10, 20, 40, 20, and 60 d for the Montreal soil. Then the standing water on top of the soil columns was removed and the columns were oriented after sealing their tops with rubber stoppers. The rubber stopper on bottom of the columns were then connected to a manifold unit for effluent. Then, 0.01 M CaCl_2 solution was pumped through the columns until Ca concentration in the effluent was approximately equal to that in the influent, i.e. when CaCl_2 completely displaced the soil solution in the columns. The soil at this stage was referred to as Ca-saturated. A total of 21 Ca saturated soil columns were

prepared (three replicates for each treatment), 18 of which were used for the column leaching test (two replicates) and six of which for the water dispersibility test.

Column leaching test

After the soil columns were saturated with Ca , the effluent in 18 of the soil columns was extracted from 0.01 M CaCl_2 solution to DOP[®] at a pumping rate of 1.25 mL per minute. The effluent from the top of each of the columns was collected with a fractionation collector. Concentrations of Fe, Al, and organic C were determined in the unfiltered and filtered (0.2 µm) effluents. The differences between the two fractions were considered as colloidal Fe, Al, and organic C. Based on preliminary experiments, colloidal Fe and Al are the major components of colloids for the Timpac soil and organic C are the major component of colloids for the blonried soil. Thus, colloidal Fe and Al, and colloidal organic C were used as approximate colloid concentrations in these two soils. Colloids were measured in colloids leached after the first 10-pore volumes was collected.

Water dispersibility test

After the soil columns were saturated with Ca , 9 soil columns (each for each treatment) was prepared for the water dispersibility test. The soil was inside the columns was shaken and not then thoroughly mixed. 1.5 g of soil for each treatment was weighed into 1.5 polycarbonate centrifuge tubes (45-mL) with half containing 45-mL of 0.01 M CaCl_2 and half containing 45-mL of 0.05 M NaCl solution. All tubes were placed in an ultrasonic system (PS20-H, Fisher Scientific) for 3 min at room temperature. Preliminary results showed that soil dispersion increased with time initially then leveled off after

reaching a maximum. After 3 minutes of sonification, 50 % of dispersible particles in both acids were dispersed (data not shown). The resulting suspensions were centrifuged (Beckman, Model 55-21) at 1000 g for 2 minutes at 30°C. This process repeatedly removes all particles > 2 µm with a particle density of 1.4 g cm^{-3} (Tanner and Jackson, 1947). The top portion of the supernatant (~20 mL) in each tube was removed carefully from the tube using a pipette. Those containing the same electrolyte solution (CaCl_2 or NaCl) were then combined to obtain two stock suspensions (~100 mL) for the dispersibility test.

A procedure to measure absorbency change of a suspension with time was developed by modifying ideas of Thillner and Spörlein (1988), Karschauer et al. (1997) and Seta and Karschauer (1997). A total of 14 polystyrene test tubes (15-mL) were used for each stock suspension. After filled with the stock suspension, these tubes were capped. A subsample of 2.0 mL was removed at 2 cm below the surface from two test tubes (duplicate) after 2, 4, 6, 8, 10, 20 and 30 h. The light absorbency of the subsamples was then read immediately at 520 nm on a Shimadzu UV 160 Spectrophotometer. All procedures were conducted under N_2 atmosphere.

Estimation of relative critical coagulation concentration (RCC)

Karim and Overbeek (1994) demonstrated the rate of coagulation of silver colloid particles from light absorbency. In a short period of time (~15 min), light scattering increases as particle sizes increase due to aggregation, and so does the reading of absorbency. This process can be described as follows based on the Rayleigh Law (Overbeek, 1952):

$$L_p = \pi V_p^2 C_p \quad (6-2)$$

$$L_t = \pi \sum_{i=1}^n V_i^2 C_i(t) \quad (6-3)$$

Where L_p , V_p and C_p are initial absorbency, average volume per particle and particle concentration, respectively. L_t , $V_i(t)$ and $C_i(t)$ are absorbency, volume and concentration of an aggregated particle consisting of i particles at time t , respectively, and n is an optical constant. For real colloids, however, their aggregation kinetics is much more complicated because of the heterogeneity in colloid composition, morphology, and size. To our knowledge, using colloid flocculation rate to estimate stability rate has not been done in literature. To estimate the overall rate of real colloid flocculation, it is necessary to measure the complicated details of real colloid aggregation with time. In our experiment, larger settling time (> 2 h) resulted in large aggregated particles settling out of the sampling zone in the test tubes via gravity, and thus the absorbency decreases with time. Obviously, the mechanism resulting in the change in light scattering (the reading of light absorbency) with time in our method is different from the one established by Hamielec and Overbeek (1994). However, assuming the size and optical constant of the aggregating particles in the sampling zone of the test tubes are constant (settling time > 2 h), the basic rationale for the method of Hamielec and Overbeek (1994) is valid in our system. In our system, $V_i(t)$ could be treated as a constant V_i , thus Eq. (5-2) can be written as:

$$L_t = \pi V^2 C(t) \quad (6-4)$$

Eq. (6-4) means that flocculation rate can be obtained by observing the rate change of absorbency with time over longer stage of flocculation.

However, we found that initial flocculation rate varied with time (see complicated results, which is similar to those reported by Farnett *et al.* (1997)). To measure uncertainty in calculating initial flocculation rate, we choose a linear regime of absorbance. Two types of absorbance-time curves were observed in our study: (1) Absorbance decreased monotonically exponentially with time at initial measurements. The rate was calculated using the slope of the linear region (3–10 s) after an initial sharp decrease in absorbance (Figure 4-1a), and (2) No distinct 'initial drop' period was detectable. The rate was determined by linear regression of the data obtained in the first 8 s of measurement (Figure 4-1b). The above procedures yield an apparent flocculation rate in the linear range. Although it is subject to error, it is useful to calculate and compare such apparent flocculation rates based on absorbance-time curves of a soil under different conditions.

Based on the definition of initial velocity rate (W) of Kramlich and Overbeek (1954), W can be expressed as follows:

$$W = C_0^2 L \left(\frac{dA}{dt} \right) \quad (4-2)$$

Where dA/dt is the slope of the absorbance-time curve in a linear stage and L is the length of the light path through the suspension. In addition, W can be measured using the ratio of the rates of rapid flocculation to slow flocculation. Rapid or final flocculation rate, in this paper, was measured using a Ca saturated soil in 0.01 M CaCl_2 electrolyte background solution. Colloids in the Ca saturated soils were mobilized when the effluent was replaced from CaCl_2 solution to DDW. However, in the absence of background electrolytes the measurement of the light absorbance in a soil suspension is subject to a

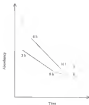


Figure 4-1 Schematic representation of typical absorbance-time curves observed. Linear regression was used to calculate an apparent flocculation rate indicated by solid line. The curves are not drawn on the same time and absorbance scales. Curve "H" stands for those obtained for the Montreal soil in 0.04 M NaCl solution, and Curve "L" for those for the Douglap soil in 0.04 M NaCl and in 0.04 M CaCl_2 solutions, and the Montreal soil in 0.04 M CaCl_2 solution.

great uncertainty. Therefore, 0.01 M NaCl solution was used as background electrolyte. Size select flocculation was then measured using Cs sedimented soil in 0.04 M NaCl background electrolyte solution. Same lower strength as both background solutions was designed to minimize the effect of soil mineral dissolution caused by electrostatic interaction between solution and mineral on soil colloid dispersion. This effect has to be considered here since the residence time of solution is much longer than that on solution leaching. Therefore, for a soil sediment after a given time, its relative RWR is defined as

$$RWR = W_{Cs}/W_{Na} = (V_0/W_0)(C_0^2/C_0^2)/(V_0/W_0)(C_0^2/C_0^2) \quad (4-6)$$

Where the subscripts Na and Cs are the measurement value in 0.01 M NaCl and 0.01 M CaCl_2 solutions, respectively. Combining Eq. (4-2) and (4-6) yields

$$RWR = (V_0/W_0)(C_0^2/C_0^2)/(V_0/W_0)(C_0^2/C_0^2) \quad (4-7)$$

Eq. (4-7) was used in this paper to estimate RWR of a soil sediment after a given time in 0.04 M NaCl solution relative to in 0.01 M CaCl_2 solution. Based on the definition above, RWR's relative magnitude represents the sediment's tendency to disperse in a soil, i.e. a larger number indicates greater tendency to be dispersed.

Results and Discussion

Figure 4-2 is a typical example of absorbance-time curves observed for the Cs-sedimented Tazuo soil in 0.01 M NaCl background electrolyte solution. The overall trend of these curves is similar to Figure 4-1b. Therefore, the slope, $(dy/dx)_{\text{max}}$ and initial absorbance (y_0), were determined from the initial linear steps (1-4 in Table 4-1) into all the parameters

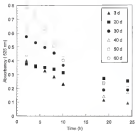


Figure 4-2 Absorbance-time curves observed at Co-irradiated Ti-sputter coil suspended in 0.01 M NaCl solution

Table 4-2 Relative rolled stability ratios (R_{R}') for two soils under different water-flooding times

S.W. & parameters	Inundation times (s) and water potential monitored (s)								
	Targeted Soil						Monitored Soil		
	1	20	30	40	50	60	1	20	30
parameters	240	110	130	40	-30	-240	230	170	60
$-d\theta/dz_{\text{top}}$	0.004	0.006	0.047	0.020	0.051	0.025	0.044	0.018	0.011
$d_z h_w$	0.40	0.30	0.38	0.46	0.61	0.79	0.56	0.40	0.18
$-d\theta/dz_{\text{bot}}$	0.011	0.009	0.028	0.024	0.041	0.05	0.081	0.008	0.015
R_{R}'	0.60	0.6	0.90	0.57	0.54	0.70	0.51	0.58	0.86

employed to calculate RW via Eq. (6-7) and RW values. Clearly, RW varied from 8.5 to 17.7 and 8.8 to 8.9 for the Tampo and Monted soils with incubation time, and reached a maximum at 30-d and 3-d, respectively (Table 6-2). This is consistent with our earlier findings (Chapter 5) that incubation significantly influences cation release from soils.

The major mechanism for dispersion of the Ca-saturated soil as the Na solution was that Ca on the X-ray layer and on the diffuse layer was displaced by Na on bulk solution, leading to electrical repulsion as a result of the EDL expansion (Ray and Durrani, 1996a). As more Na replaced Ca on the exchangeable sites, the soil became more dispersed, i.e., more colloids were released. As a result, RW, a measure of relative colloid activity, will increase with an increase in Na concentration on the exchangeable sites. This ion exchange process can be described by the Gapon-Thomson equation:

$$K_{Na-Ca} = ([Na^+]^{1/2} R_{CaO}) / ([Ca^{2+}]^{1/2} R_{NaO}) \quad (6-8)$$

Where K_{Na-Ca} is Gapon-Thomson selectivity coefficient, $[Na^+]$ and $[Ca^{2+}]$ represent Na and Ca molar concentrations, and R_{CaO} and R_{NaO} are the equivalent fractions of Ca^{2+} and Na^+ in the exchange phase of soil particles which is denoted here as X. Larger K_{Na-Ca} value indicates greater selectivity of soil exchangeable sites for Ca. Since only 1 g of Ca-saturated soil was added with 10 mL of 0.05 M NaCl solution, it is expected that $[Na^+] \gg [Ca^{2+}]$, Eq. (6-8) can be rewritten as (McBratney, 1994):

$$K_{Na-Ca} = (R_{CaO} / R_{NaO})^{1/2} (m_{Na} / m_{Ca}) M_1 \quad (6-9)$$

Where m_{Na} and m_{Ca} are moles of Ca^{2+} and Na^+ in the solution phase and M_1 is the total molarity of the solution. In our experiment, M_1 can be considered a constant. Thus, significant increase in RW (Table 6-2) at 30-d and 3-d incubation for the two soils was

most likely caused by the decrease in $\bar{G}_{\text{colloid}}/\bar{V}_{\text{colloid}}$. Therefore, Eq. (3-8) suggests that K_{colloid} cannot be constant under different coagulation times especially when there is significant change in the ratio of $\bar{G}_{\text{colloid}}/\bar{V}_{\text{colloid}}$. This is inferred by the fact that the decrease in the ratio of $\bar{G}_{\text{colloid}}/\bar{V}_{\text{colloid}}$ cannot be compensated by the increase in the ratio of $m_{\text{colloid}}/m_{\text{colloid}}$ on the right side of Eq. (3-8). It is possible that significant decrease in the selectivity coefficient K_{colloid} led to increase in RW for the two soils under different coagulation times. Thus, it seemed that RW and K_{colloid} were inversely related in this experiment. In fact, K_{colloid} is influenced by many factors such as pH, ionic strength, and exchangable ion geometry (McLachlan, 1984). However, to our knowledge, there is no substantial evidence about how coagulation time affects K_{colloid} at a soil. In addition, the heterogeneity of exchangable sites in soil colloids makes it difficult to describe the characteristics of soil particles when K_{colloid} was low. In the study and we actually measured only a small portion of the soil colloids in a soil, the heterogeneity of the soil colloids thus must be taken into account. However, with the current knowledge it is difficult to further discuss this topic with confidence. Nevertheless, high value of RW for both soils may be due to the low value of K_{colloid} , which resulted from the water-flooding condition. In Chapter 3, we suggested that the surface properties of colloid particles may be altered with coagulation, and thus changing colloid selectivity. This is consistent with the result we present here conceptually.

Comparative mobile colloids in the first 10 pore volumes in the two contaminated soils under different coagulation times were plotted against the corresponding relative colloid stability ratios (Figure 4-2). Since organic matter and Al and Fe are the major

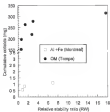


Figure 4-3: Relation of cumulative sulfide and relative stability ratio (RSR)

components of the mobile colloid in the Turpan and Bohaiwei soil, respectively, they were used to approximate the mobile colloid released from these two soils. Generally, EW was positively related to the amount of cumulative colloid (~ 10 pore volumes) in leachate for both soils (Figure 4-3). Interestingly, though the characteristics of the two soils were significantly different (Table 4-1) and colloid composition in leachate were different (majority Al/Fe vs. organic matter), the relation between cumulative colloid and EW for the two soils was similar. It is possible that the decrease in the amount of cumulative colloid with EW for the two soils in Figure 4-3 was caused by transition from dependency control to rate strength control of retaining mobile colloid as EW increased.

Our results suggest that EW may be used to predict overall colloid release in soils. However, chemically colloid release is determined by the magnitude of the energy barrier (H_{bar}), whereas colloid deposition is determined by the depth of the energy well (H_{well} , H_{well}) (Figure 2-1). Using bentonite colloids and quartz grains, Ryan and Godwin (1994) found that both colloid release rates and the magnitude of the energy barriers decreased as ionic strength increased under rapid colloid release conditions. They suggested that rapid colloid release is controlled by transport of detached colloids in the bulk solution instead of detachment itself once the energy barrier has vanished from the potential energy profile due to changes in solution chemistry. A similar phenomenon has been observed by Jacobson et al. (2007) using strict soil column experiments in which the natural particles were leached with tap water. Their results showed that particle release from the columns was not affected by an increase in flow rate. Further, their plot of accumulated amount of released particles versus square root of time shows a fairly linear

release, implying diffusion-limited kinetics is a dominant process. One candidate for this to occur is that the maximum energy barrier of mobile colloid-sediment bonds. This may be very sensitive to soil, which is consistent with the transient phenomena we discussed in Chapter 2. Under such a condition, the existing colloid concentration at a given residence time and water flow condition in a well is regulated by colloid attachment rate, i.e., the size of the energy barrier (β_{sed}). Therefore from this point of view, it can be understood that the cumulative amount of released colloid at leachate can be well related to RW, even though RW is only a measure of the magnitude of energy barrier not the depth of the energy well.

In fact, there has been considerable effort to use colloid dispersibility to predict colloid release in soil. Ragnin et al. (1986) has shown that CPC of soil colloids predicts colloid mobility reasonably well unless one strongly documents its controlling colloid deposition, which is consistent with those reported by Seta and Karickhoff (1997) and in the result presented here. However, different from CPC, the RW we defined in this paper included leachate subtractions of soil colloid flocculation when the system is subject to a perturbation in solution chemistry. In general, higher CPC indicates greater colloid stability and thus greater absorbency of suspension at a given condition. However, CPC failed to explain the colloid release in our leaching test. For example, the Tampo soil collected after 40 d has the highest average of absorbency, i.e., higher tendency for deposition (Figure 4-2), however, its cumulative colloid was almost the lowest (Table 4-2).

Conclusions

The release of soil colloids into groundwater has attracted considerable attention because of the possibility of their association with mobile contaminants. Much effort was spent to use the parameters derived from colloid deposition to predict the overall release of colloids to a soil. However, based on modern colloid theory, colloid deposition and release are different processes and thus have different dependence on the interaction between surfaces. In this chapter, we defined and estimated relative colloid mobility ratio of a Cs-contaminated soil from adsorption-desorption curves as 0.01 CaCl_2 and 0.06 NaCl [M] solutions. The uptake and slow desorption were defined as those in 0.04 CaCl_2 and 0.06 NaCl [M] solutions, respectively. There are no contact with the solution we used in the leaching test to cause error. The desorption of a Cs-contaminated soil in 0.06 NaCl [M] solution was mainly caused by cation exchange between Cs as exchangeable phase and Na as bulk solution. We inferred that the significant increase in mobility ratio for a soil with desorption was probably caused by a decrease in $K_{d,Na}$. However, the mechanism was not understood at all. Interestingly, a very obvious relation was observed that overall release of colloids from the soil increased as the mobility ratio increased, and the overall trend is similar for Tempa and bilateral soils. This result suggests that the overall release of colloids from these soils could be evaluated using the relative mobility ratio qualitatively, even though they are different conceptually.

CHAPTER 1 CONCLUSION

Metal solubility and mobility in soil

Our data showed that enhanced Pb solubility was only observed under Fe-poorest soils, for a Fe-saturated sandy soil. Similar trend was also observed using two published data sets in the literature. Since data studies this paper were from various soil morphotypes (basaltic sediment in France, Pb-contaminated soil in Poland, a sandy soil from Florida), it may be reasonable to speculate that Pb solubility may be related to Fe-poorest soils in soils.

For the two Pb-contaminated soils, metal solubility was examined by analyzing the pore waters of the incubated soil columns whereas metal mobility was examined by leaching the columns with 0.01 M CaCl₂ solution. The data showed that metal solubility in pure water and mobility with CaCl₂ solution was not always directly related. There are sufficient evidence that increases in CEC, along with Fe reduction/depletion. However, metal redistribution between solution and exchange sites with incubation is determined not only by the magnitude of CEC, but also the characteristics of metal ions, competing cations, and counter-ions (Figures).

Issues of Colloid Deposition and Release in Soil and Their Association with Heavy Metals

Soil has dominantly different features in colloid mobility compared with well-defined porous media or subsurface systems. Soil colloids are also exposed to more dynamic solution chemistry. It is therefore more difficult to predict the changes of soil

colloids since it is determined by the interactions between solid surfaces and solution. In general, soil particles are assemblages of crystalline and amorphous minerals, and organic materials. For each particle, the interface of soil particle-solution may be more practical to be described by diffuse double layer with a specific part, i.e., adsorbed surface, and a general part, i.e., a diffuse layer. The surface charge-development process may be described by partitioning of charged species between solution and solid surfaces assuming the charged species are similar. Similarly, association of heavy metals with colloids may have significant influence on colloid mobility, which is subject to dynamic changes in solution chemistry. However, very limited information is available at the present time.

Different from clays/pores media, the surfaces of soil secondary phase consist of deposited colloids. Consequently, the blocking effect of colloid-deposition on soil is significant, which may greatly enhance colloid mobility in soil compared to that in a nonparticulate clays/pores medium. Under such a condition, clay smecting is dominant mechanism in soil colloid deposition. Phenomenologically, this process is time-dependent or moisture-dependent, which is referred to as transient phenomena in colloid deposition. As the process time/water desorbible clay increased from a soil a widely used to enhance colloid mobility. However, it has to be realized that there are two simultaneous, opposite processes colloid deposition and release. In a given system, the relative effect of each on either soil clay dispersion or block test or colloid mobility in a column experiment depends on colloid resistance time.

Despite shortcomings of the DLVO (Derjagun-Landau-Verwey-Overbeek) theory, it provides a basic theoretical framework in describing soil colloid dispersion,

deposition and release, which is simple and applicable conceptually. It has to be admitted that the whole modern colloid theory (not only the DLVO-theory) has found serious difficulty in applying it to and because of heterogeneity in both structure and composition of soil particle surfaces. To determine the potential stability of soil colloid in a soil, a physicochemical approach may be more practical in the practice. Soil colloids possess high concentrations of exchangeable ions in their EDLs (high CEC). It has been long recognized that colloid release in soil is coupled by significant ion transfer between EDLs and bulk solution. Potential colloid stability may be estimated qualitatively by evaluating ion transfer.

Colloidal metal mobility in uncontaminated soils

Our results showed that colloid mobility varied greatly with conditions. For the Montmor soil, it decreased with increasing soil size, directly correlated to dissolved Fe concentrations and inversely to Ca concentrations in pore water. This must be understood by either the decreasing effect from reducing dissolution of Fe oxides and change heterogeneity along from Fe oxides. Instead, it is possible that the decrease in colloid mobility with increasing soil size was probably caused by an increase in positively-charged patches of substrate surfaces, which is determined by Ca^{2+} concentrations.

In the Montmor soil, a pattern of colloidal Fe and Al elution was observed. In general, a peak colloid release was accompanied by a greater dissolved Ca concentration. Three possible mechanisms, i.e., bulk solution displacement, diffusion out of EDL, and desorption from surfaces, were proposed to have played a major role in a time sequence on Ca release. These mechanisms may explain the pattern of changes of colloidal Al and Fe concentrations. Colloidal particles can facilitate Fe transport, however, this more

isolated with water-flooded incubation for this soil. It is possible that Pb redistribution from Fe oxides to carbonates occurred during incubation.

In addition, we defined and estimated the relative cation-selectivity ratios of a Cu-saturated, incubated soil from the desorption-rate curves in 0.01 M CaCl_2 and 0.01 M NaCl solutions. Rapid and slow desorptions were defined as those in 0.01 M CaCl_2 and 0.01 M NaCl solutions, respectively. These are consistent with the conditions used in the leaching test. The desorption of a Cu-saturated soil in 0.01 M NaCl was mainly caused by cation-exchange between Cu in exchange sites and Na in bulk solution. Significant increase in the selectivity ratio with incubation in a soil was probably caused by a decrease in the selectivity coefficient $K_{Cu,Cu}$. Interestingly, the overall release of cobalt from the soils increased as the selectivity ratio increased, and the overall trend is similar for both Thompson and Muskegon soils. These data suggest that the overall release of cobalt from these soils may be evaluated qualitatively using the relative selectivity ratios, even though they are different conceptually.

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BIOGRAPHICAL SKETCH

Yin Dong was born on September 16, 1942, in Fuchengyang Province, People's Republic of China. In P.R. China, he obtained his B.S. from the Institute of Light Industry of Qingdao in 1965. He majored in synthetic fibers engineering with a thesis titled "Synthesis of the monomer, succinyl-(polyoxepylphenylglyoxy)-esters of C_{10-14} alkyl acids and its application as a tensile softener." Then he continued his graduate education in Harbin Institute of Technology and received an M.Sc. degree in 1968, majoring in polymer materials with a thesis titled "Modification of cotton pulp paper with poly(vinyl formal) fibers both in laboratory and industry scales." In the following seven years, he worked at Department of Applied Chemistry, the Northeast Forestry University, China, on several projects with widely different subjects, such as wood-polymer composites, selective chlorination of vinylene monomers onto the celluloses, cross-cross-linking reaction for wood pulps, wooden materials treatment using rare earths, base-hydrolyzed starch-graft-polyacrylonitrile water absorbent, and cellulose preservation. Meanwhile, he enjoyed teaching courses such as general chemistry, organic chemistry, polymer chemistry, and fine chemicals and its biochemical chemistry.

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